

TITLE OF THE INVENTION

NOVEL (CO)POLYMERS AND A NOVEL POLYMERIZATION PROCESS BASED ON  
ATOM (OR GROUP) TRANSFER RADICAL POLYMERIZATION

BACKGROUND OF THE INVENTIONField of the Invention

The present invention concerns novel (co)polymers and a novel radical polymerization process based on transition metal-mediated atom or group transfer polymerization ("atom transfer radical polymerization").

Discussion of the Background

Living polymerization renders unique possibilities of preparing a multitude of polymers which are well-defined in terms of molecular dimension, polydispersity, topology, composition, functionalization and microstructure. Many living systems based on anionic, cationic and several other types of initiators have been developed over the past 40 years (see O.W. Webster, Science, 251, 887 (1991)).

However, in comparison to other living systems, living radical polymerization represented a poorly answered challenge prior to the present invention. It was difficult to control the molecular weight and the polydispersity to achieve a highly uniform product of desired structure by prior radical polymerization processes.

On the other hand, radical polymerization offers the advantages of being applicable to polymerization of a wide variety of commercially important monomers, many of which cannot be polymerized by other polymerization processes.

5 Moreover, it is easier to make random copolymers by radical polymerization than by other (e.g., ionic) polymerization processes. Certain block copolymers cannot be made by other polymerization processes. Further, radical polymerization processes can be conducted in bulk, in solution, in suspension or in an emulsion, in contrast to other polymerization processes.

10 Thus, a need is strongly felt for a radical polymerization process which provides (co)polymers having a predetermined molecular weight, a narrow molecular weight distribution (low "polydispersity"), various topologies and controlled, uniform structures.

15 Three approaches to preparation of controlled polymers in a "living" radical process have been described (Greszta et al, *Macromolecules*, **27**, 638 (1994)). The first approach involves the situation where growing radicals react reversibly with scavenging radicals to form covalent species. The second approach involves the situation where growing radicals react reversibly with covalent species to produce persistent radicals. The third approach involves the situation where growing radicals participate in a degenerative transfer reaction which regenerates the same type of radicals.

BBB  
CZ  
"SECRET"

There are some patents and articles on living/controlled radical polymerization. Some of the best-controlled polymers obtained by "living" radical polymerization are prepared with preformed alkoxyamines or are those prepared *in situ* (U.S. Patent 4,581,429; Georges et al, *Macromolecules*, **26**, 2987 (1993)). A Co-containing complex has been used to prepare "living" polyacrylates (Wayland, B. B., Pszmik, G., Mukerjee, S. L., Fryd, M. J. *Am. Chem. Soc.*, **116**, 7943 (1994)). A "living" poly(vinyl acetate) can be prepared using an Al(*i*-Bu)<sub>3</sub>: Bpy:TEMPO initiating system (Mardare et al, *Macromolecules*, **27**, 645 (1994)). An initiating system based on benzoyl peroxide and chromium acetate has been used to conduct the controlled radical polymerization of methyl methacrylate and vinyl acetate (Lee et al, *J. Chem. Soc. Trans. Faraday Soc. I*, **74**, 1726 (1978); Mardare et al, *Polym. Prep. (ACS)*, **36**(1) (1995)).

However, none of these "living" polymerization systems include an atom transfer process based on a redox reaction with a transition metal compound.

One paper describes a redox iniferter system based on Ni(0) and benzyl halides. However, a very broad and bimodal molecular weight distribution was obtained, and the initiator efficiency based on benzyl halides used was < 1% (T. Otsu, T. Tashinori, M. Yoshioka, *Chem. Express* 1990, **5**(10), 801).

Another paper describes the polymerization of methyl methacrylate, initiated by CCl<sub>4</sub> in the presence of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>.

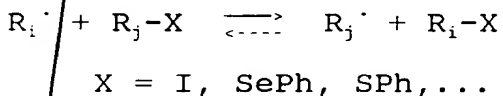
RECEIVED "2444660" 10/11/94

However, the reaction does not occur without methylaluminum bis(2,6-di-tert-butylphenoxide), added as an activator (see M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules*, **28**, 1721 (1995)). This system is similar to the redox initiators developed early (Bamford, in *Comprehensive Polymer Science (First Supplement)*, Allen, G., Aggarwal, S. L., Russo, S., eds., Pergamon: Oxford, 1991, vol. 3, p. 123), in which the small amount of initiating radicals were generated by redox reaction between (1)  $RCHX_2$  or  $RCX_3$  (where  $X = Br, Cl$ ) and (2)  $Ni(0)$  and other transition metals. The reversible deactivation of initiating radicals by oxidized  $Ni$  is very slow in comparison with propagation, resulting in very low initiator efficiency and a very broad and bimodal molecular weight distribution.

Atom transfer radical addition, ATRA, is a well-known method for carbon-carbon bond formation in organic synthesis. (For reviews of atom transfer methods in organic synthesis, see (a) Curran, D. P. *Synthesis*, **1988**, 489; (b) Curran, D. P. in *Free Radicals in Synthesis and Biology*, Minisci, F., ed., Kluwer: Dordrecht, 1989, p. 37; and (c) Curran, D. P. in *Comprehensive Organic Synthesis*, Trost, B. M., Fleming, I., eds., Pergamon: Oxford, 1991, Vol. 4, p. 715.) In a very broad class of ATRA, two types of atom transfer methods have been largely developed. One of them is known as atom abstraction or homolytic substitution (see (a) Curran et al, *J. Org. Chem.*, **1989**, 54, 3140; and (b) Curran et al, *J. Am.*

Chem. Soc., 1994, 116, 4279), in which a univalent atom (typically a halogen) or a group (such as SPh or SePh) is transferred from a neutral molecule to a radical to form a new  $\sigma$ -bond and a new radical in accordance with Scheme 1 below:

5 Scheme 1:



10 In this respect, iodine atom and the SePh group were found to work very well, due to the presence of very weak C-I and C-SePh bonds towards the reactive radicals (Curran et al, *J. Org. Chem.* and *J. Am. Chem. Soc.*, *supra*). In earlier work, the present inventors have discovered that alkyl iodides may induce the degenerative transfer process in radical polymerization, leading to a controlled radical polymerization of several alkenes. This is consistent with the fact that 15 alkyl iodides are outstanding iodine atom donors that can undergo a fast and reversible transfer in an initiation step and degenerative transfer in a propagation step (see Gaynor et al, *Polym. Prep. (Am. Chem. Soc., Polym. Chem. Div.)*, 1995, 36(1), 467; Wang et al, *Polym. Prep. (Am. Chem. Soc., Polym. Chem. Div.)*, 1995, 36(1), 465).

20 Another atom transfer method is promoted by a transition metal species (see (a) Bellus, *D. Pure & Appl. Chem.* 1985, 57, 1827; (b) Nagashima, H.; Ozaki, N.; Ishii, M.; Seki, K.;

Washiyama, M.; Itoh, K. *J. Org. Chem.* **1993**, 58, 464; (c) Udding, J. H.; Tuijp, K. J. M.; van Zanden, M. N. A.; Hiemstra, H.; Speckamp, W. N. *J. Org. Chem.* **1994**, 59, 1993; (c) Seijas et al, *Tetrahedron*, **1992**, 48(9), 1637; (d) 5 Nagashima, H.; Wakamatsu, H.; Ozaki, N.; Ishii, T.; Watanabe, M.; Tajima, T.; Itoh, K. *J. Org. Chem.* **1992**, 57, 1682; (e) Hayes, T. K.; Villani, R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1988**, 110, 5533; (f) Hirao et al, *Syn. Lett.*, **1990**, 217; and (g) Hirao et al, *J. Synth. Org. Chem. (Japan)*, **1994**, 52(3), 197; (h) Iqbal, J; Bhatia, B.; Nayyar, N. K. *Chem. Rev.*, **94**, 519 (1994)). In these reactions, a catalytic amount of transition metal compound acts as a carrier of the halogen atom in a redox process, in accordance with Figure 1.

Initially, the transition metal species,  $M_t^n$ , abstracts 15 halogen atom X from the organic halide, R-X, to form the oxidized species,  $M_t^{n+1}X$ , and the carbon-centered radical  $R^\cdot$ . In the subsequent step, the radical,  $R^\cdot$ , reacts with alkene, M, with the formation of the intermediate radical species, R-M $^\cdot$ . The reaction between  $M_t^{n+1}X$  and R-M $^\cdot$  results in the target 20 product, R-M-X, and regenerates the reduced transition metal species,  $M_t^n$ , which further reacts with R-X and promotes a new redox process.

The high efficiency of transition metal-catalyzed atom transfer reactions in producing the target product, R-M-X, in 25 good to excellent yields (often > 90%) may suggest that the presence of an  $M_t^n/M_t^{n+1}$  cycle-based redox process can

SYN  
DB  
CUB  
366000 "4874000

effectively compete with the bimolecular termination reactions between radicals (see Curran, *Synthesis*, in *Free Radicals in Synthesis and Biology*, and in *Comprehensive Organic Synthesis*, *supra*).

5 It is difficult to control the molecular weight and the polydispersity (molecular weight distribution) of polymers produced by radical polymerization. Thus, it is often difficult to achieve a highly uniform and well-defined product. It is also often difficult to control radical polymerization processes with the degree of certainty necessary in specialized applications, such as in the preparation of end functional polymers, block copolymers, star (co)polymers, etc. Further, although several initiating systems have been reported for "living"/controlled  
15 polymerization, no general pathway or process for "living"/controlled polymerization has been discovered.

Thus, a need is strongly felt for a radical polymerization process which provides (co)polymers having a predictable molecular weight and a narrow molecular weight  
20 distribution (low "polydispersity"). A further need is strongly felt for a radical polymerization process which is sufficiently flexible to provide a wide variety of products, but which can be controlled to the degree necessary to provide highly uniform products with a controlled structure (i.e.,  
25 controllable topology, composition, stereoregularity, etc.), many of which are suitable for highly specialized uses (such

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55  
60  
65  
70  
75  
80  
85  
90  
95  
100  
105  
110  
115  
120  
125  
130  
135  
140  
145  
150  
155  
160  
165  
170  
175  
180  
185  
190  
195  
200  
205  
210  
215  
220  
225  
230  
235  
240  
245  
250  
255  
260  
265  
270  
275  
280  
285  
290  
295  
300  
305  
310  
315  
320  
325  
330  
335  
340  
345  
350  
355  
360  
365  
370  
375  
380  
385  
390  
395  
400  
405  
410  
415  
420  
425  
430  
435  
440  
445  
450  
455  
460  
465  
470  
475  
480  
485  
490  
495  
500  
505  
510  
515  
520  
525  
530  
535  
540  
545  
550  
555  
560  
565  
570  
575  
580  
585  
590  
595  
600  
605  
610  
615  
620  
625  
630  
635  
640  
645  
650  
655  
660  
665  
670  
675  
680  
685  
690  
695  
700  
705  
710  
715  
720  
725  
730  
735  
740  
745  
750  
755  
760  
765  
770  
775  
780  
785  
790  
795  
800  
805  
810  
815  
820  
825  
830  
835  
840  
845  
850  
855  
860  
865  
870  
875  
880  
885  
890  
895  
900  
905  
910  
915  
920  
925  
930  
935  
940  
945  
950  
955  
960  
965  
970  
975  
980  
985  
990  
995

as thermoplastic elastomers, end-functional polymers for chain-extended polyurethanes, polyesters and polyamides, dispersants for polymer blends, etc.).

#### SUMMARY OF THE INVENTION

5           Accordingly, one object of the present invention is to provide a novel method for radical polymerization of alkenes based on atom transfer radical polymerization (ATRP), which provides a high degree of control over the polymerization process.

10           A further object of the present invention is to provide a novel method for radical polymerization of alkenes based on atom transfer radical polymerization (ATRP), which leads to more uniform and more highly controllable products (which are now obtainable only by living ionic polymerization methods).

15           A further object of the present invention is to provide a broad variety of novel (co)polymers having more uniform properties than those obtained by conventional radical polymerization.

20           These and other objects of the present invention, which will be readily understood in the context of the following detailed description of the preferred embodiments, have been provided in part by a novel process of atom (or group) radical transfer polymerization, which comprises the steps of:

25           polymerizing one or more radically polymerizable monomers in the presence of an initiator having a radically

RECEIVED "ZATHEO"

SV  
BB



transferable atom or group, a transition metal compound and a ligand to form a (co)polymer, the transition metal compound having a formula  $M_t^{n+}X'_n$ , and the ligand being any N-, O-, P- or S- containing compound which can coordinate in a  $\sigma$ -bond or any carbon-containing compound which can coordinate in a  $\pi$ -bond to the transition metal, such that direct (i.e., covalent) bonds between the transition metal and growing polymer radicals are not formed, and

isolating the formed (co)polymer;

and, in part, by novel (co)polymers prepared by atom (or group) radical transfer polymerization.

#### BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows an atom transfer method in which a catalytic amount of transition metal catalyst acts as a carrier of the halogen atom in a redox process;

Figure 2 shows a scheme for "living"/controlled radical polymerization based on a succession of atom transfer radical additions;

Figure 3 is a graph of the kinetics of methyl acrylate ("MA") bulk polymerization at 130°C, initiated with 1-phenylethyl chloride in the presence of Cu(I)Cl (1 equiv.) and bipyridine (Bpy; 3 equiv.);

Figure 4 is a graph showing that the experimental molecular weight,  $M_{n, SEC}$ , increases with monomer conversion;

Figure 5 is a graph showing that the experimental molecular weight,  $M_{n,SEC}$ , matches the theoretical molecular weight,  $M_{n,th}$ , and plotting the polydispersity,  $M_w/M_n$ , as a function of monomer conversion;

5 Figure 6 shows the correlation of the experimental molecular weights,  $M_{n,SEC}$ , with the theoretical molecular weights,  $M_{n,th}$ , for a series of bulk ATRP's of MA carried out at 130°C using various monomer/initiator molar ratios and a constant ligand/catalyst/initiator molar ratio of 3/1/1;

10 Figures 7A and 7B show the  $^1H$  NMR spectra of PST prepared at 130°C using 2-chloropropionitrile as an initiator, in the presence of 1 molar equiv. of CuCl and 3 molar equiv. of Bpy;

15 Figures 8A and 8B compare the  $^{13}C$  NMR spectra of the C=O group and the quaternary carbon atom of PMMA prepared at 100°C using methyl 2-bromoisobutyrate ("2-MiBBR"), CuBr and Bpy in a 1/1/3 molar ratio (Fig. 8A), and of PMMA prepared using a classic radical initiator, AIBN (Fig. 8B);

20 Figure 9 shows the kinetic plots of the ATRP of three typical monomers (styrene, "St", methyl acrylate, "MA", and methyl methacrylate, "MMA") using the 1/1/3 1-PECl/CuCl/Bpy initiator system, under the same experimental conditions (in bulk, at 130°C);

25 Figures 10 and 11 are graphs comparing the experimental molecular weight,  $M_{n,SEC}$ , with the theoretical molecular weight,  $M_{n,th}$ , and plotting the polydispersity,  $M_w/M_n$ , as a function of

RECEIVED "ATHEOEO

SV  
BR

monomer conversion when  $X = X' = \text{Cl}$  ("Cl ATRP"; Fig. 10) and when  $X = X' = \text{Br}$  ("Br ATRP"; Fig. 11);

Figures 12A-C show plots of  $\ln(k_p^{\text{app}})$  vs.  $\ln([1\text{-PECl}]_0)$ ,  $\ln(k_p^{\text{app}})$  vs.  $\ln([\text{CuCl}]_0)$ , and  $\ln(k_p^{\text{app}})$  vs  $\ln([\text{Bpy}]_0)$  for St ATRP in bulk at 130°C;

Figures 13A-C are graphs showing the effects of  $[\text{CuCl}]_0$  on the initiator efficiency and the molecular weight distribution for St ATRP in bulk at 130°C;

Figures 14A-B are graphs demonstrating similar results for MA ATRP;

Figure 15 is a scheme showing an overall two-electron change in which  $\text{Cu(I)Cl}$  cleaves a carbon-halogen bond to generate a  $\text{Cu(III)}$  species, followed by insertion of the alkene into the carbon-copper(III)  $\sigma$ -bond and halogen ligand transfer (reductive elimination);

Figure 16 shows a putative insertion process;

Figure 17 shows a putative process involving metal coordinated radicals; and

Figures 18A and 18B show two different mechanisms for the generation of free radicals by reacting an organic halide with a transition metal compound, involving either halogen atom transfer (Figure 18A) or outer-sphere electron transfer (Figure 18B).

5  
10  
15  
20  
330000/ATHE060

DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 The present Inventors conceptualized that if (1) the organic halide  $R-M_1-X$  resulting from an ATRA reaction is sufficiently reactive towards the transition metal  $M_2^n$  and (2) the alkene monomer is in excess, a number or sequence of atom transfer radical additions (i.e., a possible "living"/ controlled radical polymerization) may occur, as is shown in Fig. 2.

By analogy to ATRA, the present <sup>l</sup>~~I~~nventors have termed this new class of radical polymerization "atom (or group) transfer radical polymerization" (or "ATRP"), which describes the involvement of (1) the atom or group transfer pathway and (2) a radical intermediate.

Living/controlled polymerization (i.e., when chain breaking reactions such as transfer and termination are substantially absent) enables control of various parameters of macromolecular structure such as molecular weight, molecular weight distribution and terminal functionalities. It also allows the preparation of various copolymers, including block and star copolymers. Living/controlled radical polymerization requires a low stationary concentration of radicals, in equilibrium with various dormant species.

The present invention describes use of novel initiating systems leading to living/controlled radical polymerization. The initiation system is based on the reversible formation of growing radicals in a redox reaction between various

RECEIVED "PATHECO"

10

15

20

25

RE  
8/1/99

5  
BB

transition metal compounds and an initiator, exemplified by (but not limited to) alkyl halides, aralkyl halides or haloalkyl esters. Using 1-phenylethyl chloride (1-PECl) as a model initiator, CuCl as a model catalyst and bipyridine (Bpy) as a model ligand, a "living" radical bulk polymerization of styrene at 130°C affords the predicted molecular weight up to  $M_n \approx 10^5$  with a narrow molecular weight distribution (e.g.,  $M_w/M_n < 1.5$ ).

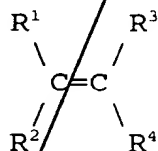
A key factor in the present invention is to achieve rapid exchange between growing radicals present at low stationary concentrations (in the range of from  $10^{-9}$  mol/L to  $10^{-6}$  mol/L, preferably  $10^{-8}$  mol/L to  $10^{-6}$  mol/L) and dormant chains present at higher concentrations (typically in the range  $10^{-4}$  mol/L to 1 mol/L, preferably  $10^{-2}$  mol/L to  $10^{-1}$  mol/L). It may be desirable to "match" the initiator/catalyst/ligand system and monomer(s) such that these concentration ranges are achieved.

Although these concentration ranges are not essential to conducting polymerization, certain disadvantageous effects may result if the concentration ranges are exceeded. For example, if the concentration of growing radicals exceeds  $10^{-6}$  mol/L, there may be too many active species in the reaction, which may lead to an undesirable increase in the rate of side reactions (e.g., radical-radical quenching, radical abstraction from species other than the catalyst system, etc.). If the concentration of growing radicals is less than  $10^{-9}$  mol/L, the rate may be undesirably slow.

10

15

25



5 wherein  $R^1$  and  $R^2$  are independently selected from the group consisting of H, halogen, CN,  $CF_3$ , straight or branched alkyl of from 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms),  $\alpha, \beta$ -unsaturated straight or branched alkenyl or alkynyl of 2 to 10 carbon atoms (preferably from 2 to 6 carbon atoms, more preferably from 2 to 4 carbon atoms),  $\alpha, \beta$ -unsaturated straight or branched alkenyl of 2 to 6 carbon atoms (preferably vinyl) substituted (preferably at the  $\alpha$ -position) with a halogen (preferably chlorine),  $C_3$ - $C_8$  cycloalkyl, heterocyclyl,  $C(=Y)R^5$ ,  $C(=Y)NR^6R^7$  and  $YC(=Y)R^8$ , where Y may be  $NR^8$  or O (preferably O),  $R^5$  is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy,  $R^6$  and  $R^7$  are independently H or alkyl of from 1 to 20 carbon atoms, or  $R^6$  and  $R^7$  may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring, and  $R^8$  is H, straight or branched  $C_1$ - $C_{20}$  alkyl or aryl; and

$R^3$  and  $R^4$  are independently selected from the group consisting of H, halogen (preferably fluorine or chlorine),  $C_1$ - $C_6$  (preferably  $C_1$ ) alkyl and  $COOR^9$  (where  $R^9$  is H, an alkali metal, or a  $C_1$ - $C_6$  alkyl group); or

$R^1$  and  $R^2$  may be joined to form a group of the formula  $(CH_2)_{n'}$  (which may be substituted with from 1 to  $2n'$  halogen

SECRETED 1/28/46

atoms or C<sub>1</sub>-C<sub>4</sub> alkyl groups) or C(=O)-Y-C(=O), where n' is from 2 to 6 (preferably 3 or 4) and Y is as defined above; and at least two of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are H or halogen.

In the context of the present application, the terms "alkyl", "alkenyl" and "alkynyl" refer to straight-chain or branched groups (except for C<sub>1</sub> and C<sub>2</sub> groups).

Furthermore, in the present application, "aryl" refers to phenyl, naphthyl, phenanthryl, phenalenyl, anthracenyl, triphenylenyl, fluoranthenyl, pyrenyl, pentacenyl, chrysenyl, naphthacenyl, hexaphenyl, picenyl and perylenyl (preferably phenyl and naphthyl), in which each hydrogen atom may be replaced with alkyl of from 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms and more preferably methyl), alkyl of from 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms and more preferably methyl) in which each of the hydrogen atoms is independently replaced by a halide (preferably a fluoride or a chloride), alkenyl of from 2 to 20 carbon atoms, alkynyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 6 carbon atoms, alkylthio of from 1 to 6 carbon atoms, C<sub>3</sub>-C<sub>8</sub> cycloalkyl, phenyl, halogen, NH<sub>2</sub>, C<sub>1</sub>-C<sub>6</sub>-alkylamino, C<sub>1</sub>-C<sub>6</sub>-dialkylamino, and phenyl which may be substituted with from 1 to 5 halogen atoms and/or C<sub>1</sub>-C<sub>4</sub> alkyl groups. (This definition of "aryl" also applies to the aryl groups in "aryloxy" and "aralkyl.") Thus, phenyl may be substituted from 1 to 5 times and naphthyl may be substituted from 1 to 7 times (preferably, any aryl group, if substituted, is substituted from 1 to 3

5  
BB  
10  
15  
20  
25  
RECEIVED "BATHED"



times) with one of the above substituents. More preferably, "aryl" refers to phenyl, naphthyl, phenyl substituted from 1 to 5 times with fluorine or chlorine, and phenyl substituted from 1 to 3 times with a substituent selected from the group consisting of alkyl of from 1 to 6 carbon atoms, alkoxy of from 1 to 4 carbon atoms and phenyl. Most preferably, "aryl" refers to phenyl, tolyl and methoxyphenyl.

In the context of the present invention, "heterocyclyl" refers to pyridyl, furyl, pyrrolyl, thienyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, pyranyl, indolyl, isoindolyl, indazolyl, benzofuryl, isobenzofuryl, benzothienyl, isobenzothienyl, chromenyl, xanthenyl, purinyl, pteridinyl, quinolyl, isoquinolyl, phthalazinyl, quinazolinyl, quinoxalinyl, naphthyridinyl, phenoxathiinyl, carbazolyl, cinnolinyl, phenanthridinyl, acridinyl, 1,10-phenanthrolinyl, phenazinyl, phenoxazinyl, phenothiazinyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, and hydrogenated forms thereof known to those in the art. Preferred heterocyclyl groups include pyridyl, furyl, pyrrolyl, thienyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, pyranyl and indolyl, the most preferred heterocyclyl group being pyridyl. Accordingly, suitable vinyl heterocycles to be used as a monomer in the present invention include 2-vinyl pyridine, 6-vinyl pyridine, 2-vinyl pyrrole, 5-vinyl pyrrole, 2-vinyl oxazole, 5-vinyl oxazole, 2-vinyl thiazole, 5-vinyl thiazole, 2-vinyl imidazole, 5-vinyl imidazole, 3-vinyl pyrazole, 5-vinyl

BB/ent  
365E020/2874E020

pyrazole, 3-vinyl pyridazine, 6-vinyl pyridazine, 3-vinyl isoxazole, 3-vinyl isothiazoles, 2-vinyl pyrimidine, 4-vinyl pyrimidine, 6-vinyl pyrimidine, and any vinyl pyrazine, the most preferred being 2-vinyl pyridine. The vinyl heterocycles mentioned above may bear one or more (preferably 1 or 2) C<sub>1</sub>-C<sub>6</sub> alkyl or alkoxy groups, cyano groups, ester groups or halogen atoms, either on the vinyl group or the heterocyclyl group, but preferably on the heterocyclyl group. Further, those vinyl heterocycles which, when unsubstituted, contain an N-H group may be protected at that position with a conventional blocking or protecting group, such as a C<sub>1</sub>-C<sub>6</sub> alkyl group, a tris-C<sub>1</sub>-C<sub>6</sub> alkylsilyl group, an acyl group of the formula R<sup>10</sup>CO (where R<sup>10</sup> is alkyl of from 1 to 20 carbon atoms, in which each of the hydrogen atoms may be independently replaced by halide [preferably fluoride or chloride]), alkenyl of from 2 to 20 carbon atoms (preferably vinyl), alkynyl of from 2 to 10 carbon atoms (preferably acetylenyl), phenyl which may be substituted with from 1 to 5 halogen atoms or alkyl groups of from 1 to 4 carbon atoms, or aralkyl (aryl-substituted alkyl, in which the aryl group is phenyl or substituted phenyl and the alkyl group is from 1 to 6 carbon atoms), etc. (This definition of "heterocyclyl" also applies to the heterocyclyl groups in "heterocyclloxy" and "heterocyclic ring.")

More specifically, preferred monomers include (meth)acrylate esters of C<sub>1</sub>-C<sub>20</sub> alcohols, acrylonitrile, cyanoacrylate esters of C<sub>1</sub>-C<sub>20</sub> alcohols, didehydromalonate

SECRETED 28742060

5  
10  
BB  
✓

5

10

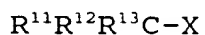
15

20

25

5 diesters of C<sub>1</sub>-C<sub>6</sub> alcohols, vinyl pyridines, vinyl N-C<sub>1</sub>-C<sub>6</sub>-  
alkylpyrroles, vinyl oxazoles, vinyl thiazoles, vinyl  
pyrimidines and vinyl imidazoles, vinyl ketones in which the  
α-carbon atom of the alkyl group does not bear a hydrogen atom  
(e.g., vinyl C<sub>1</sub>-C<sub>6</sub>-alkyl ketones in which both α-hydrogens are  
replaced with C<sub>1</sub>-C<sub>4</sub> alkyl, halogen, etc., or a vinyl phenyl  
ketone in which the phenyl may be substituted with from 1 to 5  
C<sub>1</sub>-C<sub>6</sub>-alkyl groups and/or halogen atoms), and styrenes which  
may bear a C<sub>1</sub>-C<sub>6</sub>-alkyl group on the vinyl moiety (preferably at  
the α-carbon atom) and from 1 to 5 (preferably from 1 to 3)  
substituents on the phenyl ring selected from the group  
consisting of C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl (preferably vinyl),  
C<sub>1</sub>-C<sub>6</sub>-alkynyl (preferably acetylenyl), C<sub>1</sub>-C<sub>6</sub>-alkoxy, halogen,  
nitro, carboxy, C<sub>1</sub>-C<sub>6</sub>-alkoxycarbonyl, hydroxy protected with a  
C<sub>1</sub>-C<sub>6</sub> acyl, cyano and phenyl. The most preferred monomers are  
methyl acrylate (MA), methyl methacrylate (MMA), butyl  
acrylate (BA), 2-ethylhexyl acrylate (EHA), acrylonitrile (AN)  
and styrene.

Suitable initiators include those of the formula:



where:

X is selected from the group consisting of Cl, Br, I, OR<sup>10</sup>  
(as defined above), SR<sup>14</sup>, SeR<sup>14</sup>, OC(=O)R<sup>14</sup>, OP(=O)R<sup>14</sup>,  
OP(=O)(OR<sup>14</sup>)<sub>2</sub>, OP(=O)OR<sup>14</sup>, O-N(R<sup>14</sup>)<sub>2</sub> and S-C(=S)N(R<sup>14</sup>)<sub>2</sub>, where R<sup>14</sup>

is aryl or a straight or branched  $C_1-C_{20}$  (preferably  $C_1-C_{10}$ ) alkyl group, or where an  $N(R^{14})_2$  group is present, the two  $R^{14}$  groups may be joined to form a 5-, 6- or 7-membered heterocyclic ring (in accordance with the definition of "heterocyclyl" above); and

*5*  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  are each independently selected from the group consisting of H, halogen,  $C_1-C_{20}$  alkyl (preferably  $C_1-C_{10}$  alkyl and more preferably  $C_1-C_6$  alkyl),  $C_3-C_8$  cycloalkyl,  $C(=Y)R^5$ ,  $C(=Y)NR^6R^7$  (where  $R^5-R^7$  are as defined above),  $COCl$ ,  $OH$  *10* (preferably only one of  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  is  $OH$ ),  $CN$ ,  $C_2-C_{20}$  alkenyl or alkynyl (preferably  $C_2-C_6$  alkenyl or alkynyl, and more preferably vinyl), oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl (aryl-substituted alkenyl, where aryl is as defined above, and alkenyl is vinyl which may *15* be substituted with one or two  $C_1-C_6$  alkyl groups and/or halogen atoms [preferably chlorine]),  $C_1-C_6$  alkyl in which from 1 to all of the hydrogen atoms (preferably 1) are replaced with halogen (preferably fluorine or chlorine where 1 or more hydrogen atoms are replaced, and preferably fluorine, chlorine *20* or bromine where 1 hydrogen atom is replaced) and  $C_1-C_6$  alkyl substituted with from 1 to 3 substituents (preferably 1) selected from the group consisting of  $C_1-C_4$  alkoxy, aryl, heterocyclyl,  $C(=Y)R^5$  (where  $R^5$  is as defined above),  $C(=Y)NR^6R^7$  (where  $R^6$  and  $R^7$  are as defined above), oxiranyl and glycidyl; *25* such that no more than two of  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  are H (preferably no more than one of  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  is H).

RECEIVED "4374E060"

*5/1*  
*5/1*  
*5/1*  
*5/1*  
*5/1*

In the present initiator, X is preferably Cl or Br. Cl-containing initiators generally provide (1) a slower reaction rate and (2) higher product polydispersity than the corresponding Br-containing initiators. Thus, a Br-containing initiator is most preferred.

When an alkyl, cycloalkyl, or alkyl-substituted aryl group is selected for one of  $R^{11}$ ,  $R^{12}$  and  $R^{13}$ , the alkyl group may be further substituted with an X group as defined above. Thus, it is possible for the initiator to serve as a starting molecule for branch or star (co)polymers. One example of such an initiator is a 2,2-bis(halomethyl)-1,3-dihalopropane (e.g., 2,2-bis(chloromethyl)-1,3-dichloropropane, 2,2-bis(bromomethyl)-1,3-dibromopropane), and a preferred example is where one of  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  is phenyl substituted with from one to five  $C_1$ - $C_6$  alkyl substituents, each of which may independently be further substituted with a X group (e.g.,  $\alpha, \alpha'$ -dibromoxylene, hexakis( $\alpha$ -chloro- or  $\alpha$ -bromomethyl)-benzene).

Preferred initiators include 1-phenylethyl chloride and 1-phenylethyl bromide (e.g., where  $R^{11} = \text{Ph}$ ,  $R^{12} = \text{CH}_3$ ,  $R^{13} = \text{H}$  and  $X = \text{Cl}$  or  $\text{Br}$ ), chloroform, carbon tetrachloride, 2-chloropropionitrile,  $C_1$ - $C_6$ -alkyl esters of a 2-halo- $C_1$ - $C_6$ -carboxylic acid (such as 2-chloropropionic acid, 2-bromopropionic acid, 2-chloroisobutyric acid, 2-bromoisobutyric acid, etc.) and compounds of the formula  $\text{C}_6\text{H}_x(\text{CH}_2\text{Y}')_y$ , where  $\text{Y}'$  is Cl or Br,  $x + y = 6$  and  $y \geq 1$ . More

preferred initiators include 1-phenylethyl chloride, 1-phenylethyl bromide, methyl 2-chloropropionate, ethyl 2-chloropropionate, methyl 2-bromopropionate, ethyl 2-bromoisobutyrate,  $\alpha,\alpha'$ -dichloroxylene,  $\alpha,\alpha'$ -dibromoxylene and hexakis( $\alpha$ -bromomethyl)benzene.

Any transition metal compound which can participate in a redox cycle with the initiator and dormant polymer chain, but which does not form a direct carbon-metal bond with the polymer chain, is suitable for use in the present invention.

Preferred transition metal compounds are those of the formula  $M_t^{n+}X'_n$ , where:

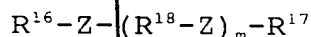
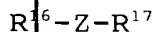
$M_t^{n+}$  may be selected from the group consisting of  $Cu^{1+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Ru^{2+}$ ,  $Ru^{3+}$ ,  $Cr^{2+}$ ,  $Cr^{3+}$ ,  $Mo^0$ ,  $Mo^+$ ,  $Mo^{2+}$ ,  $Mo^{3+}$ ,  $W^{2+}$ ,  $W^{3+}$ ,  $Rh^{3+}$ ,  $Rh^{4+}$ ,  $Co^+$ ,  $Co^{2+}$ ,  $Re^{2+}$ ,  $Re^{3+}$ ,  $Ni^0$ ,  $Ni^+$ ,  $Mn^{3+}$ ,  $Mn^{4+}$ ,  $V^{2+}$ ,  $V^{3+}$ ,  $Zn^+$ ,  $Zn^{2+}$ ,  $Au^+$ ,  $Au^{2+}$ ,  $Ag^+$  and  $Ag^{2+}$ ;

$X'$  is selected from the group consisting of halogen,  $C_1$ - $C_6$ -alkoxy,  $(SO_4)_{1/2}$ ,  $(PO_4)_{1/3}$ ,  $(HPO_4)_{1/2}$ ,  $(H_2PO_4)$ , triflate, hexafluorophosphate, methanesulfonate, arylsulfonate (preferably benzenesulfonate or toluenesulfonate),  $SeR^{14}$ , CN and  $R^{15}CO_2$ , where  $R^{14}$  is as defined above and  $R^{15}$  is H or a straight or branched  $C_1$ - $C_6$  alkyl group (preferably methyl) which may be substituted from 1 to 5 times with a halogen (preferably 1 to 3 times with fluorine or chlorine); and

$n$  is the formal charge on the metal (e.g.,  $0 \leq n \leq 7$ ).

Suitable ligands for use in the present invention include ligands having one or more nitrogen, oxygen, phosphorus and/or

sulfur atoms which can coordinate to the transition metal through a  $\sigma$ -bond, ligands containing two or more carbon atoms which can coordinate to the transition metal through a  $\pi$ -bond, and ligands which can coordinate to the transition metal through a  $\mu$ -bond or a  $\eta$ -bond. However, preferred N-, O-, P- and S- containing ligands may have one of the following formulas:



where:

$R^{16}$  and  $R^{17}$  are independently selected from the group consisting of H,  $C_1-C_{20}$  alkyl, aryl, heterocyclyl, and  $C_1-C_6$  alkyl substituted with  $C_1-C_6$  alkoxy,  $C_1-C_4$  dialkylamino,  $C(=Y)R^5$ ,  $C(=Y)R^6R^7$  and  $YC(=Y)R^8$ , where Y,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are as defined above; or

$R^{16}$  and  $R^{17}$  can be joined to form a saturated, unsaturated or heterocyclic ring as described above for the "heterocyclyl" group;

Z is O, S,  $NR^{19}$  or  $PR^{19}$ , where  $R^{19}$  is selected from the same group as  $R^{16}$  and  $R^{17}$ ,

each  $R^{18}$  is independently a divalent group selected from the group consisting of  $C_2-C_4$  alkylene (alkanediyl) and  $C_2-C_4$  alkenylene where the covalent bonds to each Z are at vicinal positions (e.g., in a 1,2-arrangement) or at  $\beta$ -positions (e.g., in a 1,3-arrangement), and from  $C_3-C_8$  cycloalkanediyl,

RECEIVED 12/14/60

5  
BB  
ent

C<sub>3</sub>-C<sub>8</sub> cycloalkenediyl, arenediyl and heterocyclylene where the covalent bonds to each Z are at vicinal positions; and

m is from 1 to 6.

5 In addition to the above ligands, each of R<sup>16</sup>-Z and R<sup>17</sup>-Z can form a ring with the R<sup>18</sup> group to which the Z is bound to form a linked or fused heterocyclic ring system (such as is described above for "heterocyclyl"). Alternatively, when R<sup>16</sup> and/or R<sup>17</sup> are heterocyclyl, Z can be a covalent bond (which may be single or double), CH<sub>2</sub> or a 4- to 7-membered ring fused to R<sup>16</sup> and/or R<sup>17</sup>, in addition to the definitions given above for Z. Exemplary ring systems for the present ligand include bipyridine, bipyrrrole, 1,10-phenanthroline, a cryptand, a crown ether, etc.

Where Z is PR<sup>19</sup>, R<sup>19</sup> can also be C<sub>1</sub>-C<sub>20</sub>-alkoxy.

15 Also included as suitable ligands in the present invention are CO (carbon monoxide), porphyrins and porphycenes, the latter two of which may be substituted with from 1 to 6 (preferably from 1 to 4) halogen atoms, C<sub>1</sub>-C<sub>6</sub> alkyl groups, C<sub>1</sub>-C<sub>6</sub>-alkoxy groups, C<sub>1</sub>-C<sub>6</sub> alkoxycarbonyl, aryl groups, 20 heterocyclyl groups, and C<sub>1</sub>-C<sub>6</sub> alkyl groups further substituted with from 1 to 3 halogens.

Further ligands suitable for use in the present invention include compounds of the formula R<sup>20</sup>R<sup>21</sup>C(C(=Y)R<sup>5</sup>)<sub>2</sub>, where Y and R<sup>5</sup> are as defined above, and each of R<sup>20</sup> and R<sup>21</sup> is 25 independently selected from the group consisting of H, halogen, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl and heterocyclyl, and R<sup>20</sup> and R<sup>21</sup> may



be joined to form a  $C_3-C_8$  cycloalkyl ring or a hydrogenated (i.e., reduced, non-aromatic or partially or fully saturated) aromatic or heterocyclic ring (consistent with the definitions of "aryl" and "heterocyclyl" above), any of which (except for H and halogen) may be further substituted with 1 to 5 and preferably 1 to 3  $C_1-C_6$  alkyl groups,  $C_1-C_6$  alkoxy groups, halogen atoms and/or aryl groups. Preferably, one of  $R^{20}$  and  $R^{21}$  is H or a negative charge.

Additional suitable ligands include, for example, ethylenediamine and propylenediamine, both of which may be substituted from one to four times on the amino nitrogen atom with a  $C_1-C_4$  alkyl group or a carboxymethyl group; aminoethanol and aminopropanol, both of which may be substituted from one to three times on the oxygen and/or nitrogen atom with a  $C_1-C_4$  alkyl group; ethylene glycol and propylene glycol, both of which may be substituted one or two times on the oxygen atoms with a  $C_1-C_4$  alkyl group; diglyme, triglyme, tetraglyme, etc.

Suitable carbon-based ligands include arenes (as described above for the "aryl" group) and the cyclopentadienyl ligand. Preferred carbon-based ligands include benzene (which may be substituted with from one to six  $C_1-C_4$  alkyl groups [e.g., methyl]) and cyclopentadienyl (which may be substituted with from one to five methyl groups, or which may be linked through an ethylene or propylene chain to a second cyclopentadienyl ligand). Where the cyclopentadienyl ligand

is used, it may not be necessary to include a counteranion (X') in the transition metal compound.

Preferred ligands include unsubstituted and substituted pyridines and bipyridines (where the substituted pyridines and bipyridines are as described above for "heterocyclyl"), acetonitrile,  $(R^{10}O)_3P$ ,  $PR^{10}$ , 1,10-phenanthroline, porphyrin, cryptands such as  $K_{22}$  and crown ethers such as 18-crown-6. The most preferred ligands are bipyridine and  $(R^{10}O)_3P$ .

In the present polymerization, the amounts and relative proportions of initiator, transition metal compound and ligand are those effective to conduct ATRP. Initiator efficiencies with the present initiator/transition metal compound/ligand system are generally very good (at least 50%, preferably  $\geq 80\%$ , more preferably  $\geq 90\%$ ). Accordingly, the amount of initiator can be selected such that the initiator concentration is from  $10^{-4}$  M to 1 M, preferably  $10^{-3}$ - $10^{-1}$  M. Alternatively, the initiator can be present in a molar ratio of from  $10^{-4}$ :1 to  $10^{-1}$ :1, preferably from  $10^{-3}$ :1 to  $5 \times 10^{-2}$ :1, relative to monomer. An initiator concentration of 0.1-1 M is particularly useful for preparing end-functional polymers.

The molar proportion of transition metal compound relative to initiator is generally that which is effective to polymerize the selected monomer(s), but may be from 0.0001:1 to 10:1, preferably from 0.1:1 to 5:1, more preferably from 0.3:1 to 2:1, and most preferably from 0.9:1 to 1.1:1. Conducting the polymerization in a homogeneous system may

permit reducing the concentration of transition metal and ligand such that the molar proportion of transition metal compound to initiator is as low as 0.001:1.

5  
10  
15  
20  
Similarly, the molar proportion of ligand relative to transition metal compound is generally that which is effective to polymerize the selected monomer(s), but can depend upon the number of coordination sites on the transition metal compound which the selected ligand will occupy. (One of ordinary skill understands the number of coordination sites on a given transition metal compound which a selected ligand will occupy.) The amount of ligand may be selected such that the ratio of (a) coordination sites on the transition metal compound to (b) coordination sites which the ligand will occupy is from 0.1:1 to 100:1, preferably from 0.2:1 to 10:1, more preferably from 0.5:1 to 3:1, and most preferably from 0.8:1 to 2:1. However, as is also known in the art, it is possible for a solvent or for a monomer to act as a ligand. For the purposes of this application, a monomer is treated as being (a) distinct from and (b) not included within the scope of the ligand.

25  
The present polymerization may be conducted in the absence of solvent ("bulk" polymerization). However, when a solvent is used, suitable solvents include ethers, cyclic ethers, C<sub>5</sub>-C<sub>10</sub> alkanes, C<sub>5</sub>-C<sub>8</sub> cycloalkanes which may be substituted with from 1 to 3 C<sub>1</sub>-C<sub>4</sub> alkyl groups, aromatic hydrocarbon solvents, halogenated hydrocarbon solvents,

RECEIVED "LBT" FEB 20 1960

10

15

20

25

5 N  
BB  
11

10 initiator ( $R^{11}$ ,  $R^{12}$  and  $R^{13}$ ) with the group(s) on the monomer ( $R^1-R^4$ ), and (2) matching the energetics of bond breaking and bond forming in dormant species (e.g., dormant polymer chains) and transition metal species (as discussed elsewhere in the specification). Matching the reactivities of the initiator with the monomer depends to some degree on the radical stabilizing effects of the substituents. Thus, where the monomer is a simple alkene or halogenated alkene (e.g., ethylene, propylene, vinyl chloride, etc.), one may select an alkyl halide initiator (e.g., where two or three of  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  are  $C_1-C_6$  alkyl). On the other hand, if one wishes to polymerize an arene- or ester-stabilized monomer (e.g., a (meth)acrylate, acrylonitrile or styrene), one may select an initiator which is stabilized by a similar group (wherein one of  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  is aryl, heterocyclyl, alkoxy carbonyl, CN, carboxyamido [ $C(=O)NR^6R^7$ ], etc.). Such "matching" of substituents on the initiator and monomer provides a beneficial balance of the relative reactivities of the initiator and monomer.

20 Preferably, the monomer, initiator, transition metal compound and ligand are selected such that the rate of initiation is not less than 1,000 times (preferably not less than 100 times) slower than the rate of propagation and/or transfer of the X group to the polymer radical. (In the present application, "propagation" refers to the reaction of a

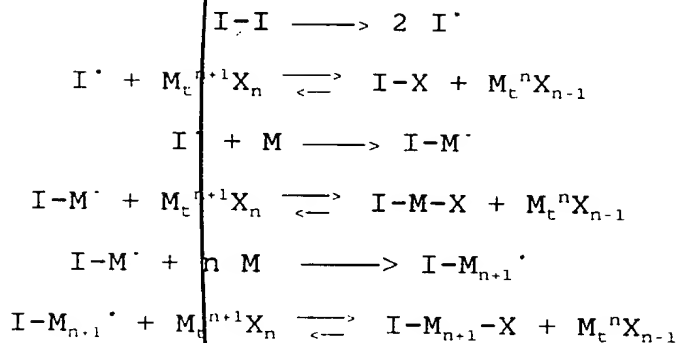
25

polymer radical with a monomer to form a polymer-monomer adduct radical.)

5  
BB  
10  
15  
20  
25  
The present polymerization may be conducted in bulk, in the gas phase (e.g., by passing the monomer in the gas phase over a bed of the catalyst which has been previously contacted with the initiator and ligand), in a sealed vessel or in an autoclave. Polymerizing may be conducted at a temperature of from -78° to 200°, preferably from 0° to 160° and most preferably from 80° to 140°. The reaction should be conducted for a length of time sufficient to convert at least 10% (preferably at least 50%, more preferably at least 75% and most preferably at least 90%) of the monomer to polymer. Typically, the reaction time will be from several minutes to 5 days, preferably from 30 minutes to 3 days, and most preferably from 1 to 24 hours. Polymerizing may be conducted at a pressure of from 0.1 to 100 atmospheres, preferably from 1 to 50 atmospheres and most preferably from 1 to 10 atmospheres (although the pressure may not be measurable directly if conducted in a sealed vessel).

One may also conduct a "reverse" ATRP, in which the transition metal compound is in its oxidized state, and the polymerization is initiated by, for example, a radical initiator such as azobis(isobutyronitrile) ("AIBN"), a peroxide such as benzoyl peroxide (BPO) or a peroxy acid such as peroxyacetic acid or peroxybenzoic acid. The radical

initiator is believed to initiate "reverse" ATRP in the following fashion:



where "I" is the initiator,  $\text{M}_t^n\text{X}_{n-1}$  is the transition metal compound, M is the monomer, and I-M-X and  $\text{M}_t^n\text{X}_{n-1}$  participate in "conventional" or "forward" ATRP in the manner described above.

After the polymerizing step is complete, the formed polymer is isolated. The isolating step of the present process is conducted by known procedures, and may comprise precipitating in a suitable solvent, filtering the precipitated polymer, washing the polymer and drying the polymer.

Precipitation can be typically conducted using a suitable  $\text{C}_5$ - $\text{C}_8$ -alkane or  $\text{C}_5$ - $\text{C}_8$ -cycloalkane solvent, such as pentane, hexane, heptane, cyclohexane or mineral spirits, or using a  $\text{C}_1$ - $\text{C}_6$ -alcohol, such as methanol, ethanol or isopropanol, or any mixture of suitable solvents. Preferably, the solvent for precipitating is hexane, mixtures of hexanes, or methanol.

5B/1

RECEIVED 12/14/60

5

10

15

20

25



or random copolymers of styrene and a (meth)acrylate or acrylonitrile may be useful thermoplastic elastomers having high solvent resistance.

5 Furthermore, block copolymers in which the blocks alternate between polar monomers and non-polar monomers produced by the present invention are useful amphiphilic surfactants or dispersants for making highly uniform polymer blends. Star polymers produced by the present process are useful high-impact (co)polymers. (For example, STYROLUX™, and anionically-polymerized styrene-butadiene star block copolymer, is a known, useful high-impact copolymer.)

10 The (co)polymers of the present invention may have a number average molecular weight of from 1,000 to 500,000 g/mol, preferably of from 2,000 to 250,000 g/mol, and more preferably of from 3,000 to 200,000 g/mol. When produced in bulk, the number average molecular weight may be up to 1,000,000 (with the same minimum weights as mentioned above). The number average molecular weight may be determined by size exclusion chromatography (SEC) or, when the initiator has a group which can be easily distinguished from the monomer(s) by NMR spectroscopy (e.g., when 1-phenylethyl chloride is the initiator and methyl methacrylate is the monomer).

20 Thus, the present invention also encompasses novel block, multi-block, star, gradient, random hyperbranched and dendritic copolymers, as well as graft or "comb" copolymers.

5N  
BB  
10  
15  
20  
25  
RECEIVED "STYROLUX"

Each of the these different types of copolymers will be described hereunder.

Because ATRP is a "living" polymerization, it can be started and stopped, practically at will. Further, the polymer product retains the functional group "X" necessary to initiate a further polymerization. Thus, in one embodiment, once the first monomer is consumed in the initial polymerizing step, a second monomer can then be added to form a second block on the growing polymer chain in a second polymerizing step. Additional polymerizations with the same or different monomer(s) can be performed to prepare multi-block copolymers.

Furthermore, since ATRP is radical polymerization, blocks can be prepared in essentially any order. One is not necessarily limited to preparing block copolymers where the sequential polymerizing steps must flow from the least stabilized polymer intermediate to the most stabilized polymer intermediate, such as is necessary in ionic polymerization. (However, as is described throughout the application, certain advantageous reaction design choices will become apparent.

However, one is not limited to those advantageous reaction design choices in the present invention.) Thus, one can prepare a multi-block copolymer in which a polyacrylonitrile or a poly(meth)acrylate block is prepared first, then a styrene or butadiene block is attached thereto, etc.

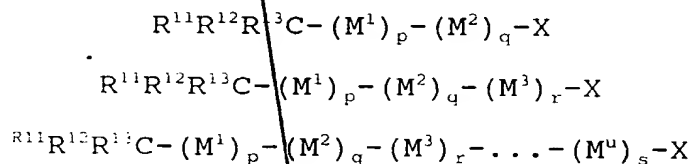
Furthermore, a linking group is not necessary to join the different blocks of the present block copolymer. One can

5  
5N  
BB  
11

10  
15  
20  
25  
30  
35  
40  
45  
50  
55  
60  
65  
70  
75  
80  
85  
90  
95  
100

simply add successive monomers to form successive blocks. Further, it is also possible (and in some cases advantageous) to first isolate a (co)polymer produced by the present ATRP process, then react the polymer with an additional monomer using a different initiator/catalyst system (to "match" the reactivity of the growing polymer chain with the new monomer). In such a case, the product polymer acts as the new initiator for the further polymerization of the additional monomer.

Thus, the present invention also encompasses block copolymers of the formula:

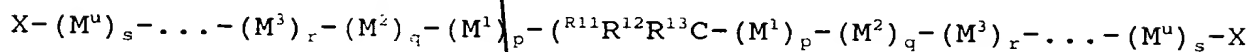


wherein  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and  $X$  are as defined above;  $M^1$ ,  $M^2$ ,  $M^3$ , ... up to  $M^u$  are each a radically polymerizable monomer (as defined above) selected such that the monomers in adjacent blocks are not identical (although monomers in non-adjacent blocks may be identical) and  $p$ ,  $q$ ,  $r$ , ... up to  $s$  are independently selected such that the number average molecular weight of each block is from 1,000 to 250,000 g/mol. After an appropriate end group conversion reaction (conducted in accordance with known methods),  $X$  may also be, for example,  $H$ ,  $OH$ ,  $N_3$ ,  $NH_2$ ,  $COOH$  or  $CONH_2$ .

SECRET "ATHEOEO"

5  
N  
B  
B  
1

5

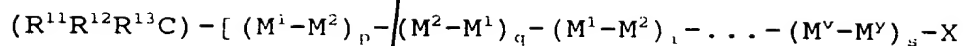


10

15

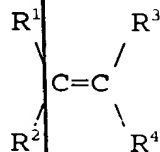
20





where  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and  $X$  are as defined for the block copolymer above,  $M^1$  and  $M^2$  are different radically-polymerizable monomers (as defined above), and  $M^v$  is one of  $M^1$  and  $M^2$  and  $M^v$  is the other of  $M^1$  and  $M^2$ . However,  $p$ ,  $q$ ,  $r$ , ... up to  $s$  are independently selected such that the number average molecular weight of the copolymer is from 1,000 to 1,000,000 g/mol, preferably from 2,000 to 250,000, and more preferably from 3,000 to 150,000 g/mol. The ratio of (1) the total number of "blocks" of statistically random units to (2) the total number of monomer units is preferably at least 1:5, more preferably at least 1:8, and most preferably at least 1:10. The present random copolymer can also serve as a block in any of the present block copolymers.

Preferably, at least one of  $M^1$  and  $M^2$  has the formula:



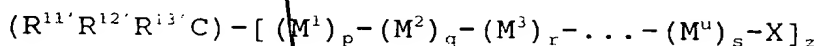
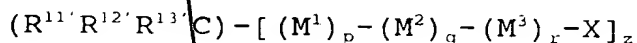
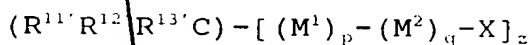
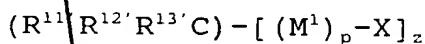
wherein at least one of  $R^1$  and  $R^2$  is CN,  $CF_3$ , straight or branched alkyl of from 4 to 20 carbon atoms (preferably from 4 to 10 carbon atoms, more preferably from 4 to 8 carbon atoms),  $C_3$ - $C_8$  cycloalkyl, aryl, heterocyclyl,  $C(=Y)R^5$ ,  $C(=Y)NR^6R^7$  and  $YC(=Y)R^8$ , where aryl, heterocyclyl,  $Y$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are as defined above; and

R<sup>3</sup> and R<sup>4</sup> are as defined above; or

R<sup>1</sup> and R<sup>3</sup> are joined to form a group of the formula C(=O)-Y-C(=O), where Y is as defined above.

More preferred monomers for the present include styrene,  
5 acrylonitrile, C<sub>1</sub>-C<sub>4</sub> esters of (meth)acrylic acid and 1,1-diphenylethylene.

5N  
BB  
10 The present invention is also useful for forming so-called "star" polymers and copolymers. Thus, where the initiator has three or more "X" groups, each of the "X" groups can serve as a polymerization initiation site. Thus, the present invention also encompasses star (co)polymers of the formula:



15 where R<sup>11'</sup>, R<sup>12'</sup> and R<sup>13'</sup> are the same as R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> with the proviso that R<sup>11'</sup>, R<sup>12'</sup> and R<sup>13'</sup> combined contain from 2 to 5 X groups; X is as defined for the block copolymer above; M<sup>1</sup>, M<sup>2</sup>,  
20 M<sup>3</sup>, ... M<sup>u</sup> are as defined above for the present block copolymers; and z is from 3 to 6.

Initiator suitable for use in preparing the present star (co)polymers are those in which the R<sup>11</sup>R<sup>12</sup>R<sup>13</sup>C group possesses at least two substituents which can be "X" (as defined above).

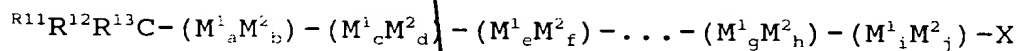
Preferably, these substituents are identical to "X". Examples of such initiators include chloroform, carbon tetrachloride, [insert examples from above]. Preferred initiators of this type include 2,2-bis(chloromethyl)-1,3-dichloropropane, 2,2-bis(bromomethyl)-1,3-dibromopropane),  $\alpha, \alpha', \alpha''$ -trichloro- and  $\alpha, \alpha', \alpha''$ -tribromocumene and hexakis( $\alpha$ -chloro- and  $\alpha$ -bromomethyl)benzene), the most preferred being hexakis( $\alpha$ -bromomethyl)benzene.

In the present copolymers, each of the blocks may have a number average molecular weight in accordance with the homopolymers described above. Thus, the present copolymers may have a molecular weight which corresponds to the number of blocks (or in the case of star polymers, the number of branches times the number of blocks) times the number average molecular weight range for each block.

The present invention also encompasses graft or "comb" copolymers, prepared by sequential ATRP's. Thus, a (co)polymer is produced by a first ATRP, in which at least one of the monomers has a  $R^1-R^4$  substituent which is encompassed by the description of the "X" group above. Preferably this substituent is Cl or Br. Examples of preferred monomers would thus include vinyl chloride, 1- or 2- chloropropene, vinyl bromide, 1,1- or 1,2-dichloro- or dibromoethene, trichloro- or tribromoethylene, tetrachloro- or tetrabromoethylene, chloroprene, 1-chlorobutadiene, 1- or 2-bromodutadiene, etc. More preferred monomers include vinyl chloride, vinyl bromide

and chloroprene. It may be necessary to hydrogenate (by known methods) a (co)polymer produced in the first ATRP of chloroprene prior to the second ATRP, using the polymer produced by the first ATRP as the initiator.

5 Gradient or tapered copolymers can be produced using ATRP by controlling the proportion of two or more monomers being added. For example, one can prepare a first block (or a oligomer) of a first monomer, then a mixture of the first monomer and a second, distinct monomer can be added in proportions of from, for example, 1:1 to 9:1 of first monomer to second monomer. After conversion of all monomer(s) is complete, sequential additions of first monomer-second monomers mixtures can provide subsequent "blocks" in which the proportions of first monomer to second monomer vary. Thus, 15 the present invention also encompasses a copolymer of the formula:



20 where  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and  $X$  are as defined for the block copolymer above,  $M^1$  and  $M^2$  are different radically-polymerizable monomers (as defined above), and  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ ,  $f$ , ... up to  $g$  and  $h$  are non-negative numbers independently selected such that  $a + b = c + d = 100$ , and any or all of  $(e + f)$ ,  $(g + h)$  and  $(i + j) = 100$  or 0, wherein the  $a:b$  ratio is from 100:0 to 0:100, the  $c:d$  ratio is from 95:5 to 5:95 (preferably from 90:10 to

5  
 10  
 15  
 20  
 25  
 30  
 35  
 40  
 45  
 50  
 55  
 60  
 65  
 70  
 75  
 80  
 85  
 90  
 95  
 100



10:90), such that  $c < a$  and  $d > b$ , and where applicable, the  
e:f ratio is from 90:10 to 10:90 (preferably from 80:20 to  
20:80), such that  $e < c$  and  $f > d$ , and depending on the number  
of blocks, the endpoints of the molar ratio ranges of first  
monomer to second monomer in successive blocks may  
progressively decrease or increase by 5 (preferably by 10)  
such that the e:f ratio is from 5:95 to 95:5 (preferably from  
10:90 to 90:10), such that  $e \neq c$  and  $f \neq d$ , and the i:j ratio  
is from 0:100 to 100:0, such that  $i \neq e$  and  $j \neq f$ .

Preferably, the proportions of first and second monomers  
in subsequent "blocks" vary by at least 10% (e.g.,  $c = a \pm 10$   
and  $b = d \pm 10$ ), preferably by at least 20%, up to 50%, from  
the preceding block. In a further embodiment, the relative  
proportions of first monomer to second monomer can be  
controlled in a continuous manner, using for example a  
programmable syringe or feedstock supply pump.

When either the initiator or monomer contains a  
substituent bearing a remote (i.e., unconjugated) ethylene or  
acetylene moiety, ATRP can be used to prepare cross-linked  
polymers and copolymers.

Polymers and copolymers produced by the present process  
have surprisingly low polydispersity for (co)polymers produced  
by radical polymerization. Typically, the ratio of the weight  
average molecular weight to number average molecular weight  
("M<sub>w</sub>/M<sub>n</sub>") is  $\leq 1.5$ , preferably  $\leq 1.4$ , and can be as low as 1.10  
or less.

Because the "living" (co)polymer chains retain an initiator fragment including X or X' as an end group, or in one embodiment, as a substituent in a monomeric unit of the polymer chain, they may be considered end-functional or in-chain functional (co)polymers. Such (co)polymers may be used directly or be converted to other functional groups for further reactions, including crosslinking, chain extension, reactive injection molding (RIM), and preparation of other types of polymers (such as polyurethanes, polyimides, etc.).

The present invention provides the following advantages:

- A larger number and wider variety of monomers can be polymerized by radical polymerization, relative to ionic and other chain polymerizations;
- Polymers and copolymers produced by the present process exhibit a low polydispersity (e.g.,  $M_w/M_n \leq 1.5$ , preferably  $\leq 1.4$ , more preferably  $\leq 1.25$ , and most preferably,  $\leq 1.10$ ), thus ensuring a greater degree of uniformity in the (co)polymer properties;
- One can select an initiator which provides an end group having the same structure as the repeating polymer units (1-phenylethyl chloride as initiator and styrene as monomer);
- The present process provides high conversion of monomer and high initiator efficiency;
- The present process exhibits excellent "living" character, thus facilitating the preparation of

- block copolymers which cannot be prepared by ionic processes;
- Polymers produced by the present process are well-defined and highly uniform, comparable to polymers produced by living ionic polymerization;
  - End-functional initiators (e.g., containing COOH, OH, NO<sub>2</sub>, etc., groups) can be used to provide an end-functional polymer in one pot;
  - The end functionality of the (co)polymers produced by the present process (e.g., Cl, Br, I, CN, CO<sub>2</sub>R) can be easily converted to other functional groups (e.g., Cl, Br and I can be converted to OH or NH<sub>2</sub> by known processes, and CN or CO<sub>2</sub>R can be hydrolyzed to form a carboxylic acid by known processes), thus facilitating their use in chain extension processes (e.g., to form long-chain polyamides, polyurethanes and/or polyesters); and
  - In some cases (e.g., where "X" is Cl, Br and I), the end functionality of the polymers produced by the present process can be reduced by known methods to provide end groups having the same structure as the repeating polymer units.

Hereinbelow, studies conducted by the present Inventors on ATRP to investigate the various parameters which affect ATRP will be described. Exemplary experimental protocols will follow.

A number of commercially available alkyl halides, R-X, combined with Cu(I)X'/Bpy, where X = X' = Cl or Br, can be used as efficient model initiator systems for the atom transfer radical polymerization (ATRP) of styrene, (meth)acrylates and other radically polymerizable monomers. The effects of various parameters in ATRP will be discussed hereinbelow to provide guidance as to the efficient control of radical polymerization.

**Atom Transfer Radical Polymerization of Styrene and (Meth)acrylates Initiated with an Alkyl Halide, R-X, and in the Presence of CuX', Complexed by 2,2'-Bipyridine.** Using 1-phenylethyl chloride (hereinafter "1-PECl") as an initiator, one molar equivalent of Cu(I)Cl as a catalyst, and three molar equivalents of 2,2'-bipyridine (hereinafter "Bpy") as a ligand (both equivalents of catalyst and ligand being relative to 1-PECl) in a model system, the so-called atom transfer radical polymerization (ATRP) of styrene (hereinafter "St") proceeds in a "living" fashion at 130°C. Similarly, using various 1:1:3 R-X:CuX':Bpy initiator systems, the atom transfer radical polymerization of styrene and various (meth)acrylates at different temperatures also affords the product polymers with the predicted molecular weight (up to  $M_n > 10^5$ ), having excellent low polydispersity (as low as 1.15; see Table 1 below).

TABLE 1

Characterization Data for ATRP of Styrene and Various (Meth)acrylates  
Initiated with RX/CuX'/Bpy<sup>a</sup>

Monomer	RX <sup>b</sup> /CuX'	T (°C)	M <sub>n, th</sub> <sup>c</sup>	M <sub>n, SEC</sub>	M <sub>w</sub> /M <sub>n</sub>
Styrene	1-PECl/CuCl	130	120,000	110,500	1.45
		100	97,000	93,300	1.50
	1-PEBr/CuBr	80	8,300	8,000	1.25
MA	2-EPNCl/CuCl	130	30,500	31,000	1.40
	2-EPNBr/CuBr	80	19,100	21,500	1.25
	2-MPNBr/CuBr	100	27,500	29,000	1.15
	$\alpha, \alpha'$ -Br <sub>2</sub> -xylene/ CuBr	100	29,500	31,000	1.25
BuA <sup>d</sup>	2-MPNBr/CuBr	130	15,000	13,500	1.50
MMA <sup>d</sup>	2-EiBBr/CuBr	100	10,000	9,800	1.40

<sup>a</sup>molar ratio of RX/CuX'/Bpy = 1/1/3; <sup>b</sup>1-PECl: 1-phenylethyl chloride, 1-PEBr: 1-phenylethyl bromide, 2-EPNCl: ethyl 2-chloropropionate, 2-EPNBr: ethyl 2-bromopropionate, 2-MPNBr: methyl 2-bromopropionate, 2-EiBBr: ethyl 2-bromoisobutyrate; <sup>c</sup>calculated according to eq. 1; <sup>d</sup> in ethyl acetate solution, 50% by volume.

As an illustrative example of the controlled character of the ATRP of (meth)acrylic esters, Figure 3 presents the kinetics of methyl acrylate ("MA") bulk polymerization at 130°C, initiated with 1-PECl in the presence of Cu(I)Cl (1 equiv.) and Bpy (3 equiv.). The straight semilogarithmic kinetic plot of  $\ln([M]_0/[M])$  vs. time ("t", in minutes) indicates that the concentration of growing radicals is constant, and that termination reactions are minimal.

Moreover, the experimental molecular weight,  $M_{n,SEC}$ , increases with monomer conversion (Figure 4) and matches the theoretical molecular weight,  $M_{n,th}$  (Figure 5), as calculated by eq. 1:

$$M_n = (\Delta[M] / [R-X]_0) \times (MW)_0 \quad (1)$$

where  $\Delta[M]$  represents the concentration of consumed monomer MA,  $[R-X]_0$  represents the initial concentration of 1-PECl, and  $(MW)_0$  represents the molecular weight of MA. These results provide evidence that 1-PECl acts as an efficient initiator, and that the number of active chains remains practically unchanged during the MA polymerization. Thus, termination and transfer side reactions, if they exist, are not significant. Both of these results suggest that the ATRP of MA is a "living" process.

Furthermore, a series of bulk ATRP's of MA was carried out at 130°C, using various monomer/initiator molar ratios,

RECEIVED "28TH" 0650

[MA]<sub>0</sub>/[1-PECl]<sub>0</sub>, and a constant ligand/catalyst/initiator molar ratio of 3/1/1. Figure 6 shows the correlation of the experimental molecular weights,  $M_{n,SEC}$ , with the theoretical molecular weights,  $M_{n,th.}$ , calculated by eq. (1). A linear plot is obtained in the molecular weight range of from  $1.5 \times 10^3$  to  $1.35 \times 10^5$ . The slope of the straight line is 0.95, thus indicating a high initiator efficiency. These results again support a "living" process of MA polymerization initiated with 1:1:3 1-PECl:CuCl:Bpy.

**End Group Analysis of Polymers Obtained by Atom Transfer Radical Polymerization.** The nature of the chain ends of low molecular weight polystyrene synthesized by the ATRP technique was analyzed by means of <sup>1</sup>H NMR spectroscopy. Figure 7 presents the <sup>1</sup>H NMR spectra of PSt which was prepared at 130°C using 2-chloropropionitrile as an initiator, in the presence of one molar equiv. of CuCl and 3 molar equiv. of Bpy. Two broad signals at 4.2-4.4 ppm are assigned to two different stereoisomers (*m* and *r*) of end group *a* in the anticipated structure 1. Moreover, two additional broad bands at 0.85 and 0.96 ppm in Figure 7 represent two stereoisomers (*m* and *r*) of the end group *d*.

Comparison of the integration values for the two end group resonances in the <sup>1</sup>H NMR spectrum (Figure 7) shows a 3:1 molar ratio of *a* and *d*. This may suggest that the St polymerization was initiated with 2-propionitrile radicals and

was efficiently deactivated with an equimolar amount of chlorine atoms (relative to the 1-propionitrile group). Moreover, comparison of the integration of the end groups with phenyl groups, *e*, at 6.5 ppm to 7.3 ppm, and to other groups, *b* and *c*, in the backbone of the polystyrene chain at 1.2 ppm to 2.5 ppm gave a molecular weight similar to the one obtained from the SEC measurement ( $M_{n, \text{NMR}} \sim 2000$  vs.  $M_{n, \text{SEC}} \sim 2100$ ), indicating a quantitative initiation by 2-chloropropionitrile. This result shows a high initiator efficiency in ATRP.

#### **Stereochemistry of Atom Transfer Radical Polymerization.**

To better understand the mechanism of ATRP, the stereochemistry of MMA polymerization was investigated.

The tacticity of poly(methyl methacrylate), PMMA, was calculated from the  $^{13}\text{C}$  NMR of the C=O group and the quaternary carbon atom, and from the  $^1\text{H}$  NMR of the  $\alpha$ -methyl group. The  $^{13}\text{C}$  NMR resonances of the C=O group and the quaternary carbon atom are recorded in the regions 175-179 ppm and 44-46.5 ppm, respectively, with respect to the reference peak of  $\text{CDCl}_3$  at 77.2 ppm. The assignment of the  $^{13}\text{C}$  signals was performed to Peat and Reynolds (see Bamford, *Reactivity, Mechanism and Structure in Polymer Chemistry*, Jenkins, A. D. and Ledwith, A., eds, John Wiley & Sons, London (1974), p. 52; and Peat et al, *Tetrahedron Lett.*, **1972**, 14, 1359).


Figure 8A displays the  $^{13}\text{C}$  NMR spectra of the C=O group and the quaternary carbon atom of PMMA prepared at 100°C using



5 methyl 2-bromoisobutyrate ("2-MiBBr"), CuBr and Bpy in a 1/1/3  
molar ratio, and Figure 8B displays the  $^{13}\text{C}$  NMR spectra of the  
C=O group and the quaternary carbon atom of PMMA prepared  
using a classic radical initiator, AIBN. Both spectra are  
almost identical. Indeed, up to a pentad sequence, PMMAs  
10 prepared using a classic radical initiator such as AIBN or BPO  
and various ATRP initiator systems have the same compositions,  
within the limits of experimental error (see Table 2 below).  
Moreover, the stereochemistry for PMMA prepared by ATRP  
appears to be consistent with a Bernoullian process, as  
indicated by a  $\rho$  value of  $\sim 1$ . These results indicate the  
presence of the same type of active species in the present  
Cu(I)X'-catalyzed polymerization and in conventional free  
radical polymerization. The similarities in stereochemistry  
15 and regiochemistry observed in the present results are  
consistent with the results observed in  $\text{Bu}_3\text{SnH}$ -mediated radical  
cyclizations and in Cu(I)-catalyzed chlorine transfer  
cyclizations reported by others (see (a) Bellus, D. *Pure &*  
*Appl. Chem.* **1985**, *57*, 1827; (b) Nagashima, H.; Ozaki, N.;  
20 Ishii, M.; Seki, K.; Washiyama, M.; Itoh, K. *J. Org. Chem.*  
**1993**, *58*, 464; (c) Udding, J. H.; Tuijp, K. J. M.; van Zanden,  
M. N. A.; Hiemstra, H.; Speckamp, W. N. *J. Org. Chem.* **1994**,  
*59*, 1993; (c) Seijas et al, *Tetrahedron*, **1992**, *48*(9), 1637).

**Effect of the Structure of the Initiator on Atom Transfer**  
25 **Radical Polymerization.** Table 3 reports the data for the ATRP

of styrene at 130°C using various commercially available alkyl chlorides, Cu(I)Cl (1 molar equiv.) and Bpy (3 molar equiv.)



RECEIVED "RESEARCH"

Table 2

Comparison of Fractions of Pentads, Triads, and Diads in Poly(methyl methacrylate) (PMMA)  
Prepared Using Classic Initiators and Various ATRP Initiator Systems

T (°C)	Initiator system	mmmm	mmmr	mmrr	rmmm + mrrm	rmrr + mrrr	rrmm	rrrr	rrrr	mm	mr	rr	m	r	$\rho^a$
130	1-PECL/CuCl/Bpy <sup>b</sup>	--	--	--	--	--	--	--	--	0.06	0.38	0.56	0.25	0.75	0.99
	BPO <sup>c</sup>	--	--	--	--	--	--	--	--	0.06	0.37	0.55	0.245	0.755	1.00
100	2-EiBBr/CuBr/Bpy <sup>d</sup>	0.01	0.03	0.04	0.11	0.26	0.06	0.22	0.27	0.05	0.36	0.59	0.23	0.77	1.04
	AIBN <sup>e</sup>	0.02	0.03	0.04	0.11	0.27	0.04	0.21	0.28	0.06	0.34	0.60	0.23	0.77	1.04
60	2-EiBBr/CuBr/Bpy <sup>d</sup>	--	--	--	--	--	--	--	--	0.04	0.33	0.63	0.205	0.795	0.99
	AIBN <sup>f</sup>	--	--	--	--	--	--	--	--	0.03	0.35	0.62	0.205	0.795	0.94

<sup>a</sup> The persistence ratio:  $\rho = 2(m)(r)/(mr)$ ; <sup>b</sup> Polymerization conditions:  $[MMA]_0 = 9.36$  M,  $[1-PECL]_0 = 0.1$  M,  $[1-PECL]_0/[CuCl]_0/[Bpy]_0 = 1/1/3$ ; <sup>c</sup> Polymerization conditions:  $[MMA]_0 = 9.36$  M,  $[BPO] = 0.1$  M; <sup>d</sup> Polymerization conditions:  $[2-EiBBr]_0 = 0.055$  M,  $[1-PECL]_0/[CuCl]_0/[Bpy]_0 = 1/1/3$ ; <sup>e</sup> Polymerization conditions:  $[MMA]_0 = 9.36$  M,  $[AIBN] = 0.1$  M; <sup>f</sup> Hatada, K. et al, *Polym. J.* 1987, 19, 413.

as initiator, catalyst, and ligand, respectively. Initiators which possess either inductive or resonance- stabilizing substituents (e.g., two or more halogen atoms in addition to the Cl transfer atom, CN, COOR, and/or aryl [Ph]) can serve as efficient mono- or bi- functional initiators (i.e, providing high initiator efficiency ["f" > 0.9] and narrow molecular weight distribution [e.g.,  $M_w/M_n \sim 1.25-1.5$ ]).

In contrast, simple alkyl chlorides as butyl chloride,  $C_4H_9Cl$ , and dichloromethane,  $CH_2Cl_2$ , do not work well with St, giving uncontrolled polymers with unexpectedly high molecular weights and broad molecular weight distribution. These results are very similar to those obtained under similar conditions in the absence of initiator (see Table 3 below). These results indicate very poor efficiency of  $C_4H_9Cl$  and  $CH_2Cl_2$  as initiators for the ATRP of St.

The results shown in Table 3 may be tentatively correlated with the carbon-halide bond strength or bond dissociation energy (BDE). For initiators having a high BDE, such as  $C_4H_9Cl$  and  $CH_2Cl_2$  (see Wang et al, *Macromolecules*, 1993, 26, 5984; and Baumgarten et al, *Macromolecules*, 1991, 24, 353), the chloride atom transfer from the initiator to  $Cu(I)Cl$  appears to be very difficult because of the strong carbon-chlorine bonds. Introduction of an inductive or resonance-stabilizing substituent into the initiator reduces the BDE of the C-Cl bond (Wang et al and Baumgarten et al, *supra*), and the generation of initiating radicals by chlorine atom

transfer becomes facile and efficient, resulting in a high initiator efficiency and narrow MWD in the ATRP of St.

TABLE 3

Styrene ATRP, Using Various Initiators in the Presence of CuCl (1 molar equiv.) and Bpy (3 molar equiv.)<sup>a</sup>

Initiator	[In'] <sub>0</sub> (10 <sup>3</sup> M)	M <sub>n,th</sub> <sup>b</sup>	M <sub>n,SEC</sub>	M <sub>w</sub> /M <sub>n</sub>
-	-	-	134,700	1.95
C <sub>4</sub> H <sub>9</sub> Cl	0.082	10,000	111,500	1.75
CH <sub>2</sub> Cl <sub>2</sub>	0.085	9,700	129,000	2.20
CHCl <sub>3</sub>	0.040	20,500	21,900	1.45
CCl <sub>4</sub>	0.047	17,600	15,500	1.30
CH <sub>3</sub> CH(Cl)CN	0.037	22,300	22,400	1.35
CH <sub>3</sub> CH(Cl)CN	0.35	2,280	2,100	1.25
CH <sub>3</sub> CH(Cl)COOC <sub>2</sub> H <sub>5</sub>	0.038	21,500	20,000	1.45
CH <sub>3</sub> CH(Cl)COOC <sub>2</sub> H <sub>5</sub>	0.65	1,210	1,290	1.35
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	0.075	11,000	10,600	1.45
ClCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	0.12	6,890	6,600	1.45

<sup>a</sup> Conversion of the polymerization: 90%-100%

<sup>b</sup> calculated based on eq. 1

In': Initiator

It must be pointed out here that the same conclusions are observed for ATRP of other monomers, such as MA and MMA.

**Effect of the Polymer Structure,  $M_n$ , and the Polymeric Halide,  $M_n-X'$ , on Atom Transfer Radical Polymerization.** Figure 9 illustrates the kinetic plots of the ATRP of three typical monomers, St, MA, and MMA, using the same initiator system 1-PEC1/CuCl/Bpy (1/1/3), under the same experimental conditions, in bulk and at 130°C.

The slopes of the straight kinetic plots in Figure 9 allow the calculation of the apparent propagation rate constants ( $k_p^{app}$ ) in the ATRP of St, MA and MMA. Furthermore, knowing the corresponding thermodynamic parameters,  $A_p$  and  $E_p$ , one can estimate the absolute propagation rate constants at various temperatures,  $k_p'$ , and the stationary concentrations of growing radicals,  $[P']_{st}$ , according to equations (5) and (6), respectively:

$$R_p = -d[M]/dt = k_p' \times [M] \times [P']_{st} \quad (2)$$

For each system described herein,  $[P']_{st}$  can be considered constant. Therefore:

$$-d[M]/dt = k_p' \times [M] \times [P']_{st} = k_p^{app} \times [M] \quad (3)$$

and

$$\ln([M]_0/[M]) = k_p^{app} \times t \quad (4)$$

$$\ln(k_p') = \ln(A_p) - (E_p/RT) \quad (5)$$

$$[P']_{st} = k_p^{app}/k_p' \quad (6)$$

Table 4 shows the kinetic data and estimated concentrations of growing radicals in bulk ATRP of St, MMA, and MA initiated with 1-PECl/CuCl/Bpy (1/1/3) at 130°C. The concentration of growing radicals decreases in the order  $[P']_{MMA} > [P']_{st} \approx [P']_{MA}$ .

TABLE 4

Kinetic Data and Estimated Concentration of Growing Radicals  $[P']$ , for Bulk ATRP of St, MA, and MMA Initiated with 1-PECl/CuCl/Bpy (1/1/3) at 130°C

Monomer	MA	MMA	St
$[1-PECl]_0$ (mol/l)	0.038	0.038	0.038
$[M]_0$ (mol/l)	11.1	9.36	8.7
$k_p'$ , 130°C ( $10^3$ mol/l s <sup>-1</sup> )	14.1 <sup>a</sup>	3.17 <sup>b</sup>	6.87 <sup>c</sup>
$k_p^{app}$ , 130°C ( $10^{-4}$ s <sup>-1</sup> )	3.14	5.83	1.35
$[P']$ ( $10^{-7}$ M)	0.22	1.84	0.19

<sup>a</sup>:  $\ln k_{p,MA} = 18.42 - (3574/T)$ , see Odian, G. *Principles of Polymerization*, Wiley-Interscience, New York, 1991;

<sup>b</sup>:  $\ln k_{p,MMA} = 14.685 - (2669/T)$ , see Hutchinson et al,

*Macromolecules*, **1993**, 26, 6410; <sup>c</sup>:  $\ln k_{p,St} = 16.786 - (3204/T)$ , see Hutchinson et al, *supra*.

Effect of the Transfer Atom (Leaving Group),  $X'$ , on Atom Transfer Radical Polymerization. Since the atom transfer process reflects the strength of the bond breaking and bond forming in  $M_n-X'$ , it is expected that the leaving group,  $X'$ , will strongly affect control of the atom transfer reaction.

From Table 5, it can be noted that ATRP is essentially faster when  $X$  is bromine as compared to when  $X$  is chlorine. This can be explained by the presence of more growing radicals in the polymerization process when  $X$  is bromine as compared to when  $X$  is chlorine.

The effect of the leaving group,  $X$ , on the living character of the polymerization is also significant. For instance, in MA polymerizations at  $100^\circ\text{C}$  using the same molar ratio of initiator/ $\text{CuX}$ /Bpy and the same initiating radical, ethyl propionate, at high monomer conversions (e.g.,  $> 50\%$ ) the experimental molecular weight,  $M_{n,\text{SEC}}$ , and is very close to the theoretical molecular weight,  $M_{n,\text{th}}$ , when  $X = X' = \text{either Br or Cl}$ . However, at relatively low conversions (e.g.,  $< 50\%$ ), the discrepancy between  $M_{n,\text{SEC}}$  and  $M_{n,\text{th}}$  is much larger when  $X = X' = \text{Cl}$  ("Cl ATRP") as compared to when  $X = X' = \text{Br}$  ("Br ATRP") (see Figures 10 and 11).

Moreover, the polydispersity of resulting polymers obtained by Cl ATRP is usually larger than the polydispersity obtained by Br ATRP (e.g., an  $M_w/M_n$  of 1.15-1.35 vs. 1.30-1.50; see Figures 10 and 11).



**Table 5**  
**The Effect of the Leaving Group, X, on Kinetics**  
**of ATRP at Different Temperatures<sup>a</sup>**

Monomer	T, °C	ATRP	$k_p^{app}$	$k_p^*$	$[P^*]$
			$10^{-5} s^{-1}$	$10^3 mol/l$	$10^{-9} mol/l$
MMA	80	Cl ATRP	~ 1.71	1.24	13.8
		Br ATRP	~ 3.52	1.24	28.4
MA	80	Cl ATRP	b	4.01	-
		Br ATRP	~ 1.28	4.01	3.19
	100	Cl ATRP	1.45	6.89	2.10
		Br ATRP	3.47	6.89	5.02
St	80	Cl ATRP	b	2.23	-
		Br ATRP	~ 1.45	2.23	6.50

<sup>a</sup> 1 - PCl and 1 - PBr were used as Initiators for Cl and Br ATRP, respectively,  $[1 - PEX]_0 = 0.1M$ , and  $[1 - PEX]_0 / [CuX]_0 / [Bpy]_0 = 1 / 1 / 3$ ; b no polymer can be detected in 40 hrs.

09034487 020398

Effect of the Concentrations of the Components in Initiator System, R-X/CuX/Bpy, on Atom Transfer Radical Polymerization. In order to gain a better understanding of the ATRP mechanism, the effects of the components in the initiator system compositions on the kinetics and the living character of polymerization were investigated.

As discussed in the previous sections, the slope of the kinetic semilogarithmic anamorphoses allows the calculation of apparent rate constant  $k_p^{app}$ , and thus the external orders in initiator, catalyst, and ligand, can be determined:

$$k_p^{app} = d(\ln[M])/dt = k[RX]_0^x \times [CuX]_0^y \times [Bpy]_0^z \quad (7)$$

and

$$\ln(k_p^{app}) = \ln(k) + x\ln([RX]_0) + y\ln([CuX]_0) + z\ln([Bpy]_0) \quad (8)$$

The plots of  $\ln(k_p^{app})$  vs.  $\ln([1-PECl]_0)$ ,  $\ln(k_p^{app})$  vs.  $\ln([CuCl]_0)$ , and  $\ln(k_p^{app})$  vs.  $\ln([Bpy]_0)$  for St ATRP in bulk at 130°C are given in Figures 12A-C. The fraction orders observed in these graphs are approximately 1, 0.4, and 0.6 for  $[1-PECl]_0$ ,  $[CuCl]_0$ , and  $[Bpy]_0$ , respectively. The first order of  $k_p^{app}$  in initiator,  $[1-PECl]_0$ , is expected. However, since the systems studied were heterogenous, it is difficult to give precise physical meanings for 0.4 and 0.6 orders in  $[CuCl]_0$  and  $[Bpy]_0$ , respectively.

5 The effects of the compositions of the components in  
initiator system on the living character of the above-  
described ATRP of St reveal several important features. As  
seen from Figure 13, there appear to be no significant effects  
of  $[\text{CuCl}]_0$  on the initiator efficiency and the molecular weight  
distribution. Indeed, even in the presence of 0.3 molar  
equiv. of CuCl relative to 1-PECl, the experimental molecular  
weight,  $M_{n, \text{SEC}}$ , still linearly increases with monomer conversion  
and is close to the theoretical molecular weight obtained by  
means of eq. 1 (Figure 13A). The similar results are also  
found for MA (Figures 5 and 14). These findings suggest that  
in ATRP, the CuX acts as a catalyst and the addition of  
catalytic amount of CuX complexed by Bpy is sufficient to  
promote a controlled ATRP, even in these heterogeneous  
15 systems.

**Transition Metal Catalyzed-Atom Transfer Radical Addition  
and Transition Metal Catalyzed-Atom Transfer Radical  
Polymerization.** As described above, atom transfer radical  
polymerization, ATRP, can be considered as a succession of  
consecutive atom transfer radical additions, ATRA's. The  
prerequisite for a successful transformation of transition  
metal catalyzed-ATRA to transition metal catalyzed-ATRP is  
that a number of polymeric halides,  $M_n\text{-X}$ , can be effectively  
activated by  $M_t^n$  (Fig. 2). Present work demonstrates that a  
20

Cu(I)/Cu(II)-based redox process in the presence of Bpy can achieve that goal.

Indeed, to prevent possible polymerization and to obtain the monomeric adduct, R-M-X, in good to excellent yields in the ATRA process, organic chemists often use either (1) activated organic halogens as radical sources, (2) terminal alkenes without resonance-stabilizing substituents or (3) both activated organic halogens as radical sources and terminal alkenes without resonance-stabilizing substituents (see (a) Bellus, D. *Pure & Appl. Chem.* **1985**, 57, 1827; (b) Nagashima, H.; Ozaki, N.; Ishii, M.; Seki, K.; Washiyama, M.; Itoh, K. *J. Org. Chem.* **1993**, 58, 464; (c) Udding, J. H.; Tuijp, K. J. M.; van Zanden, M. N. A.; Hiemstra, H.; Speckamp, W. N. *J. Org. Chem.* **1994**, 59, 1993; (c) Seijas et al, *Tetrahedron*, **1992**, 48(9), 1637; (d) Nagashima, H.; Wakamatsu, H.; Ozaki, N.; Ishii, T.; Watanabe, M.; Tajima, T.; Itoh, K. *J. Org. Chem.* **1992**, 57, 1682; (e) Hayes, T. K.; Villani, R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1988**, 110, 5533; (f) Hirao et al, *Syn. Lett.*, **1990**, 217; and (g) Hirao et al, *J. Synth. Org. Chem. (Japan)*, **1994**, 52(3), 197; (h) Iqbal, J; Bhatia, B.; Nayyar, N. K. *Chem. Rev.*, **94**, 519 (1994)). Under such conditions, the further generation of free radicals, R-M $\cdot$ , is kinetically less favorable, since R-M-X is much less reactive than R-Y towards the transition metal species, M $_t^n$  (Fig. 1).

From the results described herein, the following parameters appear to be important to promote the successful

transformation of ATRA to ATRP. First, the use of suitable ligands (e.g., Bpy,  $P(OEt)_3$ ) increases the solubility of the transition metal compound (e.g.,  $CuX$ ) by coordination, can facilitate the abstraction of a halogen atom from the initiator, and more importantly, can facilitate abstraction of the transfer atom or group from the dormant polymeric halide,  $R-M_n-X$ , with the formation of initiating and growing radicals (Fig. 2). Secondly, as demonstrated in Table 3, the presence of either inductive or resonance stabilizing substituents in the initiator are beneficial for generating initiating radicals,  $R^\cdot$ , in growing PSt and PMMA chains. Finally, in practice, the use of a high polymerization temperature is beneficial, particularly for Cl ATRP (Table 5). In fact, many ATRA processes also appear to use rather high temperatures.

Prior to the present invention,  $RuCl_2(PPh_3)_3$  was known to promote only the monomeric addition of  $CCl_4$  to alkenes. Very recently, it was reported that  $RuCl_2(PPh_3)_3$  induced the controlled radical polymerization of MMA at  $60^\circ C$  in the presence of methylaluminum bis(2,4-di-tert-butylphenoxide) (Sawamoto et al, *Macromolecules*, 1995, 28, 1721). However, the present inventors observed that at high polymerization temperatures (e.g.,  $130^\circ C$ , a number of radically polymerizable monomers undergo ATRP in the absence of methylaluminum bis(2,4-di-tert-butylphenoxide) or other such activators. As a result, one may increase polymerization temperature (rather than include methylaluminum bis(2,4-di-tert-butylphenoxide) or

other activator) as a means to enhance the reactivity of less reactive monomeric or polymeric halides towards transition metal species with the formation of propagation radicals. Indeed, it is possible that an activator may lead to a change in the polymerization mechanism.

**Radical Addition vs Coordination Insertion.** Regarding the mechanism of ATRP, the important question to be answered is whether the ATRP really involves radical intermediates during polymerization.

The generation of radical intermediates by reacting some transition metal species, including salts and/or complexes of copper, ruthenium, iron, vanadium, niobium, and others, with alkyl halides, R-X, is well documented (see (a) Bellus, D. *Pure & Appl. Chem.* **1985**, 57, 1827; (b) Nagashima, H.; Ozaki, N.; Ishii, M.; Seki, K.; Washiyama, M.; Itoh, K. *J. Org. Chem.* **1993**, 58, 464; (c) Udding, J. H.; Tuijp, K. J. M.; van Zanden, M. N. A.; Hiemstra, H.; Speckamp, W. N. *J. Org. Chem.* **1994**, 59, 1993; (c) Seijas et al, *Tetrahedron*, **1992**, 48(9), 1637; (d) Nagashima, H.; Wakamatsu, H.; Ozaki, N.; Ishii, T.; Watanabe, M.; Tajima, T.; Itoh, K. *J. Org. Chem.* **1992**, 57, 1682; (e) Hayes, T. K.; Villani, R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1988**, 110, 5533; (f) Hirao et al, *Syn. Lett.*, **1990**, 217; and (g) Hirao et al, *J. Synth. Org. Chem. (Japan)*, **1994**, 52(3), 197; (h) Iqbal, J; Bhatia, B.; Nayyar, N. K. *Chem. Rev.*, **94**, 519 (1994); and Kochi, J.K., *Organometallic*

*Mechanisms and Catalysis*, Academic Press, New York, 1978, and references cited therein). Moreover, it is also known that R-X/transition metal species-based redox initiators, such as  $\text{Mo}(\text{CO})_6/\text{CHCl}_3$ ,  $\text{Cr}(\text{CO})_5/\text{CCl}_4$ ,  $\text{Co}_4(\text{CO})_{12}/\text{CCl}_4$ , and  $\text{Ni}[\text{P}(\text{OPh})_3]_4/\text{CCl}_4$ , promote radical polymerization (see Bamford, *Comprehensive Polymer Science*, Allen, G., Aggarwal, S. L., Russo, S., eds., Pergamon: Oxford, 1991, vol. 3, p. 123). The participation of free radicals in these redox initiator-promoted polymerizations was supported by end-group analysis and direct observation of radicals by ESR spectroscopy (see Bamford, *Proc. Roy. Soc.*, 1972, A, 326, 431).

However, different transition metal species may act in a different manner. They may induce an atom transfer reaction or provide a source of metal-complexed radicals or even initiate a catalytic cycle that does not involve radical intermediates (Curran et al, *J. Org. Chem.* and *J. Am. Chem. Soc.*, *supra*).

In fact, several examples using additives such as  $\text{CuX}$ , a catalyst suitable for the present invention, reported previously showed that the reactions between some polyhaloalkanes, e.g.,  $\text{CCl}_4$ , and alkenes exceptionally lead to exclusive 1:1 adducts in many cases (Bellus, *supra*). The authors argued that, if radical addition were the case, a considerable amount of telomer formation would be expected even at high organic polyhalide/alkene ratios. Thus, they questioned whether  $\text{Cu(I)Cl}$  cleaves the carbon-halogen bond by

an atom transfer process to generate a carbon radical and a Cu(II) species (Fig. 2) or by an overall two-electron change to generate a Cu(III) species 2 (Fig. 15), followed by insertion of the alkene into the carbon-copper(III)  $\sigma$ -bond and halogen ligand transfer (reductive elimination) with a new Cu(III) species 3 formed.

In sharp contrast to previous observations, the present invention shows that the polymerization of alkenes occurs when halide initiators, including  $\text{CCl}_4$ , are used with CuX complexed by Bpy as a catalyst. The uncomplexed CuX species may not be powerful enough to abstract the halogen atom from the 1:1 monomeric adduct to promote atom transfer radical polymerization. As described below, the polymerization of St initiated with 1-PECl/CuCl without ligand is an ill-controlled, thermally self-initiated polymerization.

Moreover, the similarities in stereochemistry of the polymerizations of MMA initiated with classic radical initiators and various initiator/CuX/Bpy systems (Table 2) suggests that a putative insertion process (Fig. 16) can be rejected. Although metal coordinated radicals (Fig. 17) may be involved in the polymerizations of alkenes initiated with the R-X/CuX/Bpy system, a simple radical process is most probable (Fig. 2). The participation of the free radical intermediates is also supported by the observation that addition of 1.5 molar equiv. of galvinoxyl (relative to 1-PECl) effectively inhibits polymerization, and no styrene

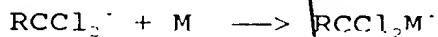


polymerization was initiated with 1-PECl/CuCl/Bpy (1/1/3) within 18 hours. Further evidence for the presence of radical intermediated in ATRP is the fact that the monomer reactivity ratios for ATRP random copolymerization resembles the monomer reactivity ratios for classical radical polymerization processes (i.e.,  $r_{MMA} = 0.46/r_{St} = 0.48$  for ATRP at 100°C initiated with 2-EiBBr/CuBr/Bpy, and  $r_{MMA} = 0.46/r_{St} = 0.52$  for radical polymerization initiated with BPO at 60°C).

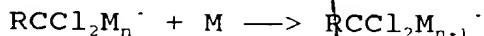
**Atom Transfer Radical Polymerization vs. Redox Radical Telomerization.** It is well known that radical telomerization can be initiated by a transition metal species-based redox catalyst. The mechanism is generally described as shown below:

Scheme 2

Initiation:



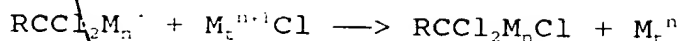
Propagation:



Chain Transfer:



Termination:



5 The fundamental differences between ATRP and redox radical telomerization are as follows. In ATRP, the polymeric halides,  $\text{R-M}_n\text{-X}$ , behave as *dormant* species (Fig. 2). They can be repeatedly activated by transition metal species,  $\text{M}_t^n$ , to form the growing radicals,  $\text{R-M}_n^{\cdot}$ , and oxidized transition metal species,  $\text{M}_t^{n+1}$ , which can further react with  $\text{R-M}_n^{\cdot}$  to regenerate  $\text{R-M}_n\text{-X}$  and  $\text{M}_t^n$ , i.e., a *reversible* transfer process.

10 Contrary to ATRP, redox radical telomerization represents a *degradative* transfer process, in which the resulting polymeric halides,  $\text{R-M}_n\text{-X}$ , are *dead* chains (see Scheme 2 above). Consequently, the molecular weight obtained in redox radical telomerization does not increase with the monomer conversion, whereas the molecular weight increases linearly with increasing monomer conversion in ATRP.

#### Factors Affecting Atom Transfer Radical Polymerization.

20 (a) "Living"/Controlled Radical Polymerization. To better describe controlled ATRP, a discussion of some general properties for "living"/controlled radical polymerization is in order.

Free radicals, which are the growing species in radical polymerization, are highly reactive species. Unlike anions or cations, they recombine and/or disproportionate at rates

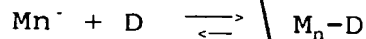
05034187 030398

approaching the diffusion controlled limit (i.e.,  $k_t$  of about  $10^8-10^{10} \text{ M}^{-1} \cdot \text{sec}^{-1}$ ), which is much higher than the corresponding propagating rate constant (i.e.,  $k_p \sim 10^{2-4} \text{ M}^{-1} \cdot \text{sec}^{-1}$ ).

Moreover, initiation is incomplete due to slow decomposition of classic radical initiator (i.e.,  $k_d \sim 10^{-4-6} \text{ sec}^{-1}$ ). These are the kinetic reasons why classic radical polymerization yields ill-defined polymers with unpredictable molecular weight, broad molecular weight distribution, and uncontrolled structures.

Moreover, due to the same kinetic reasons, it is impossible to entirely suppress the termination reactions and to obtain a *living* radical polymerization, in which chain breaking (termination) reactions are absent (Szwarc, *Nature*, 1956, 176, 1168). Thus, for the sake of the accuracy, we propose the term *controlled* or "*living*" radical polymerization to describe the processes in which the side reactions are not significant. Consequently, structural parameters, such as molecular dimension, molecular weight distribution, composition, topology, functionality, etc., can be controlled to some extent.

The preparation of controlled polymers in a "living" radical process requires a low stationary concentration of growing radicals,  $M_n^{\cdot}$ , which are in a fast dynamic equilibrium with the dormant species,  $M_n-D$ :



Termination is second order and propagation is first order in respect to growing radicals (eqs. (12) and (13):

$$R_p = d(\ln[M])/dt = k_p[M] \times [P\cdot] \quad (12)$$

$$R_t = -d[P\cdot]/dt = k_t \times [P\cdot]^2 \quad (13)$$

At low concentration of free radicals, the proportion of termination versus propagation is reduced. If the reversible exchange between growing radicals,  $M_n\cdot$ , and dormant species,  $M_n-D$ , is fast, the polymerization degree can be predetermined by the ratio of the concentration of the consumed monomer to that of the dormant chains (eq. 14), and the molecular weight distribution may remain narrow.

$$DP_n = \Delta[M]/[M_n-D] = \Delta[M]/[I]_0 \quad (14)$$

Recent progress in controlled radical polymerization can be indeed related to the approach illustrated in the  $M_n-D$  reaction above, in which growing radicals,  $M_n\cdot$ , react reversibly with species D, which may be carbon-, sulfur-, and oxygen-centered radicals (Otsu et al, *Makromol. Chem, Rapid Commun.*, **1982**, 127; Otsu et al, *Macromolecules*, **1992**, 25, 5554; Bledzki et al, *Makromol. Chem*, **1983**, 184, 745; Druliner, *Macromolecules*, **1991**, 24, 6079; U.S. Patent No. 4,581,429; and Georges et al, *Macromolecules*, **1993**, 26, 2987), alkylaluminum complexes (Mardare et al, *Macromolecules*, **1994**, 27, 645), and

organocobalt porphyrin complexes (Wayland, B. B., Pszmik, G., Mukerjee, S. L., Fryd, M. J. *Am. Chem. Soc.*, **1994**, 116, 7943), in a reversible deactivated process. Another approach (discovered by the present inventors) is based on using alkyl iodides in a degenerative transfer.

**The Significance of the Presence of the Low Concentration of Growing Radicals in Maintaining "Living" ATRP.** Since ATRP promoted by the Cu(I)/Cu(II) redox process resembles classic radical polymerization, termination reactions can not completely eliminated, which are second order in respect to growing radicals (eq. 13). As already discussed in the preceding section, if the concentration of growing radicals is kept low enough, and a fast and reversible equilibrium between growing radicals and dormant species is established (see Scheme 2 above), the proportion of termination in comparison to propagation can be minimized, resulting in a predictable molecular weight and a narrow molecular weight distribution. Indeed, this is the case for "living" ATRP.

Table 6 lists the estimated polymerization time for 90% monomer conversion,  $t_{0.9}$ , concentration of the dead polymer chains due to the spontaneous termination reactions at that time,  $[P]_{d,0.9}$ , concentration of the polymer chains due to self-initiation,  $[P]_{self,0.9}$ , and percentage of uncontrolled polymer chains generated by side reactions, "UC", in bulk ATRP of St, MMA, and MA initiated with 1-PECl/CuCl/Bpy at 130°C:

$$\ln ([M]_0/[M]) = \ln (10) = k_p^{app} \times t_{0.9} \quad (15)$$

$$[P]_{t,0.9} = R_t \times t_{0.9} \quad (16)$$

$$[P]_{self,0.9} = R_{i,self} \times t_{0.9} \quad (17)$$

$$"UC" = ([P]_{self,0.9} + [P]_{d,0.9}) / \{[R-X]_0 + [P]_{self,0.9} + [P]_{d,0.9}\} \quad (18)$$

Table 6

Estimated  $[P]$ ,  $t_{0.9}$ ,  $[P]_{self,0.9}$ ,  $[P]_{d,0.9}$ , and "UC"  
for Bulk ATRP of St, MMA and MA Initiated with  
1-PECl/CuCl/Bpy (1/1/3) at 130°C

Monomer	MA	MMA	St
$[1-PECl]_0$ (mol/l)	0.038	0.038	0.038
$[M]_0$ (mol/l)	11.1	9.36	8.7
$k_{p,130^\circ C}$ (M s <sup>-1</sup> ) <sup>a</sup>	14,100	3170	6870
$k_{t,130^\circ C}$ (10 <sup>7</sup> s <sup>-1</sup> ) <sup>b</sup>	1.98	0.31	0.532
$k_p^{app,130^\circ C}$ (10 <sup>-4</sup> s <sup>-1</sup> )	3.14	5.83	1.35
$[P]$ (10 <sup>-7</sup> M) <sup>a</sup>	0.22	1.84	0.19
$t_{0.90}$ (s <sup>-1</sup> )	7300	4000	17100
$[P]_{d,0.90}$ (10 <sup>-4</sup> mol/l)	0.7	4.20	1.22
$[P]_{self,0.90}$ (10 <sup>-3</sup> mol/l)	--	--	1.7
"UC", %	0.2	1.1	4.5

<sup>a</sup>: see Table 4; <sup>b</sup>: Data from Odian, G. *Principles of Polymerization*, Wiley-Interscience, John Wiley & Sons, New York, 1991;  $\ln k_{t,MA} = 23.43 - (2671/T)$ ,  $\ln k_{t,MMA} = 18.5 - (1432/T)$ ,  $\ln k_{t,St} = 17.47 - (962/T)$ .

As shown in Table 6, at 90% monomer conversion, the concentrations of uncontrolled polymer chains, "UC", are all less than 3% in ATRP's of St, MMA, and MA, when 1-PECl/CuCl/Bpy (1/1/3) is used as the initiator system at 130°C. This may be why ATRP proceeds in a "living" manner. Although the termination rate constant is larger in MA radical polymerization than in the other two processes, ATRP of MA is better controlled than ATRPs of St and MMA. This appears to be due to a lower concentration of growing radicals in the ATRP of MA (Table 6).

**The Significance of the Presence of Fast Exchange Between  $R-M_n-X$  and  $R-M_n\cdot$  in Inducing Low Polydispersity in ATRP.** At a low concentration of radicals (Tables 4-6), ca.  $10^{-7}$  to about  $10^{-8}$  mol/l, polymers with very high and uncontrolled molecular weights are usually found. To cope with this problem, a reversible equilibrium between a minute amount of growing, radicals and a large amount of the dormant species needs to be established. Moreover, only if both (1) the initiation reaction between initiating radicals and monomer and (2) the exchange reaction between the growing radicals and the dormant species are faster than (3) the propagation reaction between the growing radicals and the monomer, the molecular weight of the resulting polymers can be predicted by eq. (14), and low polydispersity polymers can be obtained.

Moreover, in a so-called "living" system with reversible dynamic exchange, there is evidence that the polydispersity of the resulting polymers largely depends on the ratio of the deactivation rate to the propagation rate (Matyjaszewski, K. Polym. Prep. (Am. Chem. Soc. Polym. Chem. Div.), 1995, 36(1), 541). On the other hand, it has been demonstrated that many transition metal species can be used as efficient retarders or inhibitors in radical polymerization (Bamford, Comprehensive Polymer Science, Allen, G., Aggarwal, S. L., Russo, S., eds., Pergamon: Oxford, 1991, p. 1). For example, the reaction rate constants between (1) PSt<sup>•</sup> and CuCl<sub>2</sub> and (2) PMMA<sup>•</sup> radicals and CuCl<sub>2</sub> are 10<sup>4</sup> and 10<sup>3</sup> times greater in comparison with the corresponding propagation rate constants, respectively.

Therefore, the existence of a fast deactivation (scavenging) reaction can explain the low polydispersity obtained in ATRP.

Earlier, Otsu et al reported that an R-Cl/Ni(0) combined initiator system can induce a "living" radical polymerization of St and MMA at 60°C (Chem. Express, 1990, 5(10), 801).

However, the "living" character of the R-Cl/Ni(0) combined initiator of Otsu et al may not be entirely accurate, since (1) the molecular weight of the obtained polymers did not increase linearly with respect to monomer conversion, (2) the initiator efficiency is low (about 1% based on R-Cl), and (3) the molecular weight distribution is broad and bimodal. The same phenomena were also observed by the present inventors.

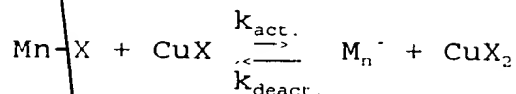


Thus, it appears that the R-Cl/Ni(0) combined initiator of Otsu et al does not provide controlled polymers.

Based on the published evidence, the R-Cl/Ni(0) combined initiator of Otsu et al appears to act as a conventional redox initiator, similar to the initiators developed by Bamford (see *Reactivity, Mechanism and Structure in Polymer Chemistry*, Jenkins, A. D. and Ledwith, A., eds, John Wiley & Sons, London (1974), p. 52; and *Comprehensive Polymer Science*, Allen, G., Aggarwal, S. L., Russo, S., eds., Pergamon: Oxford, 1991, vol. 3, p. 123). The very low initiator efficiency and a broad, bimodal molecular weight distribution observed in the system of Otsu et al suggests that in that system, the small amount of initiating radicals were generated by a redox reaction between R-Cl and Ni(0), and the reversible deactivation of initiating radicals by oxidized Ni species is inefficient in comparison to propagation. This may support the idea that fast exchange between R-X and R $\cdot$  in transition metal-promoted ATRP at the initial step is one of the key factors controlling initiator efficiency and molecular weight distribution.

**The Factors Affecting the Concentrations of the Growing Radicals and the Exchange Rate Between R-M<sub>n</sub>-X and R-M<sub>n</sub> $\cdot$  in ATRP.** Based on the results shown herein, the factors affecting the concentrations of the growing (initiating) radicals and the exchange rate between R-M<sub>n</sub>-X (R-X) and R-M<sub>n</sub> $\cdot$  (R $\cdot$ ) in ATRP can be qualitatively discussed.

The stationary concentration of growing radicals can be expressed as in eq. (20):



$$K = k_{\text{act.}}/k_{\text{deact.}} = ([\text{M}_n^{\cdot}] \times [\text{CuX}_2])/([\text{Mn-X}] \times [\text{CuX}]) \approx [\text{M}_n^{\cdot}]^2/([\text{R-X}]_0 \times [\text{CuX}]_0) \quad (19)$$

$$[\text{M}_n^{\cdot}] = \{(k_{\text{act.}}/k_{\text{deact.}}) \times ([\text{R-X}]_0 \times [\text{CuX}]_0)\}^{1/2} \quad (20)$$

An increase in  $[\text{R-X}]_0$  and  $[\text{CuX}]_0$  results in an increase in the concentration of growing radicals, and subsequently, in the polymerization rate (Figure 12).

As also seen from eq. (20), the concentration of growing (initiating) radicals is proportional and inversely proportional to the activation and deactivation rate constants, respectively, which strongly depend on the structure of the  $\text{R}^{11}\text{R}^{12}\text{R}^{13}\text{C}$  group in the initiator, the structure of the repeating monomer units M in  $\text{R-M}_n\text{-X}$ , the leaving group X, and the polymerization temperature (see Tables 3, 4 and 5, Figure 9).

In terms of polarity, the deactivation reaction between  $\text{PMA}^{\cdot}$  and  $\text{CuCl}_2$  is usually 10 times slower than that between  $\text{Pst}^{\cdot}$  and  $\text{CuCl}_2$  (i.e.,  $k_{\text{deact. Pst}^{\cdot}/\text{CuCl}_2} > k_{\text{deact. PMA}^{\cdot}/\text{CuCl}_2}$ ) (see Bamford, *Comprehensive Polymer Science*, Allen, G., Aggarwal, S. L., Russo, S., eds., Pergamon: Oxford, 1991, p. 1). Thus, the similar concentration of radicals found in the ATRP of St

relative to the ATRP of MA indicates that the activation reaction between CuCl and PSt-Cl is faster than the one between PMA-Cl and CuCl (i.e.,  $k_{\text{act. PSt-Cl}} > k_{\text{act. PMA-Cl}}$ ). This is in good agreement with the lower bond dissociation energy in PSt-Cl as compared to PMA-Cl (see Danen, W. C., in *Methods in Free Radical Chemistry*, Huyser, E. L. S., ed., Dekker, New York, 1974, vol. 5, p.1; and Poutsma, *supra*). The higher concentration of growing radicals found in the ATRP of MMA as compared to the ATRP's of St and MA (see Table 4) implies that steric hindrance in both the polymeric halide PMMA-Cl and growing radical PMMA $\cdot$  may significantly affect deactivation and activation rates.

As noted in Figures 10 and 11, the polymerization is much faster in the Br-ATRP of MA than in the Cl-ATRP of MA, due to a higher stationary concentration of radicals in the former system as compared to the latter one. However, the polydispersity is much narrower in Br ATRP than in Cl-ATRP. According to the discussion in the preceding section, this suggests that deactivation of free radicals with CuBr<sub>2</sub> is faster in comparison to deactivation of free radicals with CuCl<sub>2</sub>. Since the concentration of growing radicals in Br-ATRP is larger than in Cl-ATRP (see Table 5), the activation of PMA-Br by Br-containing Cu(I) species must be faster than the activation of PMA-Cl by Cl-containing Cu(I) species. This is also in accordance with the fact that the ease of the abstraction of X from R-X by CuX follows the order Br > Cl

(i.e., the lower the bond dissociation energy in R-X, the easier to abstract an X atom; see Curran, *Synthesis*, in *Free Radicals in Synthesis and Biology*, and in *Comprehensive Organic Synthesis*; Danen; and Poutsma, all *supra*).

5        **Halogen Atom Transfer (Abstraction) vs. Outer-Sphere Electron Transfer.** The generation of free radicals by reacting an organic halide with a transition metal compound may involve two different mechanisms: either halogen atom transfer (Figure 18A) or outer-sphere electron transfer (Figure 18B). The former process depends on the carbon-halogen bond dissociation energy, whereas the latter is a function of the electrode potential for the reaction of the organic halide (i.e.,  $RX + e^- \rightarrow R^\cdot + X^-$ ).

10  
15        The outer sphere electron transfer process is usually less sensitive than halogen atom transfer to the leaving atom X in R-X and to temperature (Howes et al, *Inorg. Chem.* **1988**, 27, 3147; and references therein). As discussed before, the results presented herein show that transition metal mediated ATRP has a strong dependence on the leaving group X in R-X, as well as on the reaction temperature. Thus, the results herein suggest that ATRP involves a direct atom transfer process.

20  
25        Alternatively, the reversible conversion of the radicals  $R^\cdot$  and  $R-M_n^\cdot$  to organic halides R-X and  $R-M_n-X$  may involve direct atom transfer (see Kochi, J.K., *Organometallic Mechanisms and Catalysis*, Academic Press, New York, 1978, and

09034487 020398

intermediates (see Kochi, *supra*; Orochov, A., Asscher, M., Vofsi D. *J. Chem. Soc., Perkin II.* 1973, 1000; and Mitani, M., Kato, L., Koyama, K. *J. Am. Chem. Soc.* 1983, 105, 6719).

Thus a successful extension of atom transfer radical addition, ATRA, to atom transfer radical polymerization, ATRP has been demonstrated in a Cu(I)/Cu(II) model redox process.

The present process opens a new pathway to conduct a "living" or controlled radical polymerization of alkenes. The controlled process found in ATRP results from two important contributions: (1) a low stationary concentration of growing radicals and (2) a fast and reversible equilibrium between the growing radicals and the dormant species. Many parameters, such as the nature of transition metals, the structure and property of ligands, the polymerization conditions, etc, may affect the course of "living" ATRP. On the other hand, it is anticipated that, like other controlled polymerizations, ATRP will provide a powerful tool for producing various tailor-made polymers.

Other features of the present invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention, and are not intended to be limiting thereof.

## EXAMPLES

### Example 1:

An aralkyl chloride, 1-phenylethyl chloride, 1-PECl, is an efficient initiator, and a transition metal halide, CuCl, complexed by 2,2'-bipyridine, bpy, is an efficient chlorine atom transfer promoter. This model initiating system affords controlled polymers with predicted molecular weight and narrower molecular weight distribution,  $M_w/M_n < 1.5$ , than obtained by conventional free radical polymerization.

Phenylethyl chloride, 1-PECl, was prepared according to a literature procedure (Landini, D.; Rolla, F. *J. Org. Chem.*, **1980**, 45, 3527).

A typical polymerization was carried out by heating a reddish brown solution of styrene (St), 1-PECl (0.01 molar equiv. relative to monomer), CuCl (1 molar equiv. relative to 1-PECl), and bpy (3 molar equiv. relative to CuCl), in a glass tube sealed under vacuum at 130°C. (The reddish brown color of a slightly heterogeneous solution was formed within 30 seconds at 130°C.) The formed polymer was then dissolved in THF and precipitated in MeOH (three times), filtered and dried at 60°C under vacuum for 48 hr. Yield, 95%. A linear

increase in the number average molecular weight,  $M_{n,SEC}$ , versus monomer conversions up to 95% was found for PMA.  $M_{n,SEC}$  values were determined by size exclusive chromatography, and were calibrated using polystyrene standards.

5 The  $M_{n,SEC}$  is very close to the theoretical one,  $M_{n,th}$ , calculated by the following equation (21):

$$M_{n,th} = ([M]_0/[1-PECl]_0) \times (MW)_0 \times \text{conversion} \quad (21)$$

10  $[M]_0$  and  $[1-PECl]_0$  represent the initial concentrations of monomer (St) and 1-PECl, respectively, and  $(MW)_0$  is the molecular weight of monomer. These results indicate that 1-PECl acts as an efficient initiator, and that the number of the chains is constant. The molecular weight distribution is fairly narrow ( $M_w/M_n = 1.3-1.45$ ). The linear plot of  $\ln([M]_0/[M])$  versus polymerization time (e.g., Figure 3) 15 implies that the concentration of growing radicals remains constant during propagation, and that termination is not significant. Both of these results suggest a "living" polymerization process with a negligible amount of transfer and termination.

20 Additionally, a series of experiments has been carried out at 130°C, using various  $[M]_0/[1-PECl]_0$  ratios and a constant  $[1-PECl]_0/[CuCl]_0/[bpy]_0$  ratio of 1:1:3. Similar to Figure 5, a graph was prepared which compares the  $M_{n,SEC}$  and calculated  $M_{n,th}$ , based on equation (21) above.

09034187 030398  
B6EED 28T2E5D

A linear plot is observed in the molecular weight range from  $3.8 \times 10^3$  to  $1.05 \times 10^5$  g/mol. The slope of the straight line is 0.93, indicating a high initiator efficiency. The polydispersities of all the polymers obtained also remain low and are smaller than in a conventional radical polymerization i.e.,  $M_w/M_n < 1.5$ . These results again support a "living" polymerization process initiated with 1-PECl/CuCl/Bpy system.

Table 7 summarizes the results of styrene polymerization under various experimental conditions. In the absence of 1-PECl, CuCl or bpy, the polymers obtained are ill-controlled with unpredictable molecular weights and with broad molecular weight distributions.

09034187-030333



Table 7

Results of Styrene Bulk Polymerization at 130°C

[St] <sub>0</sub> (mmol)	Conv. (%)	[1-PECl] <sub>0</sub> (mmol)	[CuCl] <sub>0</sub> (mmol)	[byp] <sub>0</sub> (mmol)	M <sub>n,th.</sub> <sup>a</sup>	M <sub>n,SEC</sub>	M <sub>w</sub> /M <sub>n</sub>
4.375	15	0	0	0	0	132,100	1.76
4.375	52	0	0.182	0.54	0	134,700	1.95
4.375	40	0.0528	0.0455	0	3,400	68,700	3.10
4.40	45	0.0528	0	0.135	4,100	76,500	2.10

<sup>a</sup> calculated based on eq. 21

Example 2:

The same initiating system, 1-PECl/CuCl/Bpy (1/1/3), can be also used for the controlled polymerization of acrylic monomers, such as methyl methacrylate, MMA, methyl acrylate, MA, and butyl acrylate, BA. Block copolymers of St and MA have been produced using the same technique as described in Example 1 for homopolymerization of styrene (see the Examples below). Heating of chlorine atom end-capped polystyrene (0.5 g,  $M_n = 4000$ ,  $M_w/M_n = 1.45$ ) and a two-fold excess of MA (1.0 g) in the presence of 1 molar equiv. of CuCl and 3 molar equiv. of bpy (both relative to polystyrene) at 130°C results in MA block polymerization to form the desired PSt-b-PMA block copolymer (yield: 95%,  $M_n = 13,000$ ,  $M_w/M_n = 1.35$ ).

Discussion

By analogy with transition metal catalyzed atom transfer radical addition reactions (ATRA), used in organic synthesis, the results presented herein can be explained by the mechanism shown in Fig. 2. The present process appears to involve a succession of ATRA processes, and therefore, can be called atom transfer radical polymerization, ATRP.

The model catalyst Cu<sup>I</sup>Cl acts as a carrier of the chlorine atom in a redox reaction between Cu(I) and Cu(II). The coordination of the bidentate nitrogen ligand to Cu<sup>I</sup>Cl increases the solubility of the inorganic salt and can also affect the position of the redox equilibrium, so as to

facilitate the abstraction of a chlorine from the initiator, 1-PECl, and the dormant species,  $P_i\text{-Cl}$ , with the formation of initiating and growing radicals, respectively. The reversible conversion of radicals,  $R^\cdot$  and  $P_i^\cdot$ , to the corresponding halides,  $R\text{-Cl}$  and  $P_i\text{-Cl}$ , may involve a direct atom transfer reaction (Kochi, J.K. *Organometallic Mechanisms and Catalysis*, Academic Press: New York, 1978, and references therein; Asscher, M., Vofsi, D. *J. Chem. Soc., Perkin II*. 1968, 947; Cohen, H., Meyerstein, D. *Inorg. Chem.* 1974, 13, 2434) or oxidative addition/reductive elimination with the formation of the organocopper (III) intermediates (Kochi, supra; Orochov, A., Asscher, M., Vofsi D. *J. Chem. Soc., Perkin II*. 1973, 1000; Mitani, M., Kato, L., Koyama, K. *J. Am. Chem. Soc.* 1983, 105, 6719). If the concentration of growing radicals is low and the redox reaction is fast compared to bimolecular reactions of the radicals, the extent of the termination reactions is minimized, resulting in a "living" process. Moreover, if the rate of reversible exchange between  $P_i\text{-Cl}$  and  $P_i^\cdot$  is comparable to that of propagation, the number average molecular weight should be defined by eq. (21), and the molecular weight distribution should remain narrow.

Two observations support the participation of free radicals in ATRP. First, the tacticity of the polymers is similar to those synthesized by typical radical initiators. For example, the tacticity of poly(methyl methacrylate)  $M_n =$

35,400,  $M_w/M_n = 1.40$ ) synthesized using a 1-PECl/CuCl/Bpy  
initiator system (in a 1:1:3 molar ratio) at 130°C is  
rr/mr(rm)/mm: 53/38/9. These values are very close to those  
of PMMA prepared using a typical radical initiator, BPO, at  
the same temperature. Therefore, the organocuprate(III)  
species, if it exists, probably does not react directly with  
monomer, otherwise some effect on tacticity would be expected.  
Secondly, addition of 1.5 molar equiv. of galvinoxyl (relative  
to 1-PECl) effectively inhibits the polymerization. In the  
presence of galvinoxyl, no styrene polymerization was found  
within 18 hours.

The low proportion of termination, despite the relatively  
rapid polymerization, may be explained by stabilizing  
interactions between radicals  $P_i^\cdot$  and  $CuCl_2$ . It may be  
possible that the monomer reacts with a radical  $P_i^\cdot$  within a  
solvent cage, in which the ratio of rate constants of  
propagation to termination is higher than for uncomplexed  
radicals in solution.

At 130°C, styrene may polymerize thermally by self-  
initiation. (Moad, G., Rizzardo, E., Solomon, D. H. *Polym.*  
*Bull.*, 1982, 6, 589). The contribution of this reaction in  
ATRP is rather small, because (1) ATRP is fast and (2) the  
relative rate of self-initiation is further reduced with the  
progress of the reaction. However, the small contribution of  
self-initiation may enhance polydispersities to the range of

$M_w/M_n \approx 1.4$ , and may reduce molecular weights to slightly lower values than theoretically predicted.

It must be stressed that the present transition-metal promoted ATRP, in which the molecular weight linearly increases with monomer conversion, is very different from typical redox radical telomerization promoted by transition metal species in which the molecular weight does not increase with conversion (Boutevin, B., Pietrasant, Y., in *Comprehensive Polymer Science*, Allen, G., Aggarwal, S. L., Russo, S., eds., Pergamon: Oxford, 1991, vol. 3. p 185; Bamford, C. H., in *Comprehensive Polymer Science (First Supplement)*, Allen, G., Aggarwal, S. L., Russo, S., eds., Pergamon: Oxford, 1991, p. 1).

In conclusion, the model alkyl chloride initiator, 1-PECl, and model transition metal complex CuCl/bpy polymerize styrene by repetitive atom transfer radical additions to give well-defined high molecular weight polymers with narrow molecular weight distributions.

For examples 3-22, the polymers were isolated by either of two procedures:

- (1) The polymer was dissolved in THF and precipitated in MeOH (three times), filtered and dried under vacuum; or
- (2) The heterogeneous reaction solution was filtered, and the solvent was removed under vacuum.

Removal of solvent or drying can optionally be conducted using mild heat (e.g., 25-60°C). The same polymeric product is obtained, regardless of the isolation procedure.

Monomers, and ethyl acetate were vacuum-distilled over  $\text{CaH}_2$  before use.  $\text{CuCl}$  and  $\text{CuBr}$  were purified according to the known procedures (see Nagashima, H.; Ozaki, N.; Ishii, M.; Seki, K.; Washiyama, M.; Itoh, K. *J. Org. Chem.* **1993**, *58*, 464; (c) Udding, J. H.; Tuijp, K. J. M.; van Zanden, M. N. A.; Hiemstra, H.; Speckamp, W. N. *J. Org. Chem.* **1994**, *59*, 1993; (c) Seijas et al, *Tetrahedron*, **1992**, *48*(9), 1637; (d) Nagashima, H.; Wakamatsu, H.; Ozaki, N.; Ishii, T.; Watanabe, M.; Tajima, T.; Itoh, K. *J. Org. Chem.* **1992**, *57*, 1682).

Example 3:

Polystyrene was prepared by heating styrene (0.9 g), 1-phenylethyl chloride (1  $\mu\text{L}$ ,  $7.54 \times 10^{-6}$  mol),  $\text{Cu(I)Cl}$  ( $7.54 \times 10^{-6}$  mol) and 2,2'-bipyridine (Bpy;  $2.26 \times 10^{-5}$  mol) at 130° in a sealed tube for 21.5 h. The polymerization reaction mixture was then dissolved in THF, and precipitated in methanol. The precipitated polymer was filtered, and the dissolving, precipitating and filtering steps were repeated two additional times. The obtained polymer was dried at 60°C under vacuum for 48 h.

The dried polymer had a number average molecular weight as measured by size exclusion chromatography (SEC),  $M_{\text{nSEC}}$ , of 95,000, in good agreement with the theoretical number average

molecular weight,  $M_{n,th.}$ , of 102,000. The dried polymer was obtained in 85% yield. The polydispersity,  $M_w/M_n$ , was 1.45.

Example 4:

5 Polystyrene was prepared according to the procedure described in Example 3, except polymerization was conducted at 100°C for 88 h. The polymer was obtained in 80% yield. The  $M_{n,SEC}$  of 93,300 was in excellent agreement with the  $M_{n,th.}$  of 97,000. The  $M_w/M_n$  of the obtained polymer was 1.50.

Example 5:

10 The procedure of Example 3 was repeated, except that 0.45 g of styrene and 2.5  $\mu$ L ( $1.89 \times 10^{-5}$  mol) of 1-PECl were employed, Ni(0) ( $2.73 \times 10^{-5}$  mol) was used as the transition metal in place of Cu(I)Cl, and  $PPh_3$  ( $1.41 \times 10^{-4}$  mol) was used as the ligand in place of Bpy. The reaction was conducted at 15 130°C for 12 h.

The polymer was obtained in 85% yield. The  $M_{n,SEC}$  of the obtained polymer was 129,000 ( $M_{n,th.} = 17,000$ ), and the  $M_w/M_n = 1.70$ .

Example 6:

20 Polystyrene was prepared according to the procedure of Example 3, except that the concentration of 1-PECl was  $2.26 \times 10^{-5}$  mol (amount = 3  $\mu$ L),  $RuCl_2$  ( $2.26 \times 10^{-5}$  mol) was used in place of Cu(I)Cl, and  $PPh_3$  ( $6.78 \times 10^{-5}$  mol) was used in place

of Bpy. The polymerization was conducted at 130°C for 13.5 h. The polymer was obtained in 90% yield. The  $M_{n,SEC}$  of 18,300 was in excellent agreement with the  $M_{n,th.}$  of 17,900. The obtained polymer had an  $M_w/M_n$  of 2.0.

5 Example 7:

6  
7  
8  
9  
10 Polystyrene was prepared according to the procedure of Example 3, except that AIBN ( $1.7 \times 10^{-5}$  mol) was used in place of 1-PECI, Cu(II)Cl<sub>2</sub> ( $3 \times 10^{-5}$  mol) was used in place of Cu(I)Cl, and Bpy was present in a molar amount of  $7 \times 10^{-5}$  mol. The polymerization was conducted at 130°C for 5 h. The polymer was obtained in 90% yield. The  $M_{n,SEC}$  of 18,500 was in agreement with the  $M_{n,th.}$  of 25,000. The obtained polymer had an  $M_w/M_n$  of 1.7.

15 Example 8:

16  
17  
18  
19  
20 Polystyrene was prepared according to the procedure of Example 3, except that 2-chloropropionitrile ( $3.75 \times 10^{-6}$  mol) was used in place of 1-PECI; Cu(I)Cl and Cu(II)Cl<sub>2</sub> were used in an equimolar mixture ( $3.76 \times 10^{-6}$  mol of each) in place of Cu(I)Cl alone; and Bpy was present in a molar amount of  $1.9 \times 10^{-5}$  mol. The polymerization was conducted at 130°C for 33 h. The polymer was obtained in 80% yield. The  $M_{n,SEC}$  of 81,500 was in good agreement with the  $M_{n,th.}$  of 95,500. The obtained polymer had an  $M_w/M_n$  of 1.4.

RECEIVED "RESEARCH"



Example 9:

Polystyrene was prepared according to the procedure of Example 3, except that benzyl chloride ( $3.75 \times 10^{-5}$  mol) was used in place of 1-PECl,  $\text{FeCl}_2$  ( $3.75 \times 10^{-5}$  mol) was used in place of  $\text{Cu(I)Cl}$ , and  $(\text{EtO})_3\text{P}$  ( $1.15 \times 10^{-4}$  mol) was used in place of Bpy. The polymerization was conducted at  $130^\circ\text{C}$  for 5.5 h. The polymer was obtained in 85% yield. The  $M_{n,\text{SEC}}$  of 19,300 was in good agreement with the  $M_{n,\text{th}}$  of 21,100. The obtained polymer had an  $M_w/M_n$  of 3.0.

Example 10:

Poly(methyl acrylate), PMA, was prepared according to the procedure of Example 3, except that 1.45 grams of MA were used,  $\alpha,\alpha'$ -dibromoxylene ( $4.4 \times 10^{-5}$  mol) was used in place of 1-PECl,  $\text{Cu(I)Br}$  ( $8 \times 10^{-5}$  mol) was used in place of  $\text{Cu(I)Cl}$ , and Bpy was present in a molar amount of  $2.5 \times 10^{-4}$  mol. The polymerization was conducted at  $80^\circ\text{C}$  for 36 h. The polymer was obtained in 90% yield. The  $M_{n,\text{SEC}}$  of 31,000 was in very good agreement with the  $M_{n,\text{th}}$  of 29,500. The obtained polymer had an  $M_w/M_n$  of 1.2.

Example 11:

Poly(methyl acrylate) was prepared according to the procedure of Example 10, except that 0.48 g of MA were used, 2-methylbromopropionate ( $1.47 \times 10^{-5}$  mol) was used in place of  $\alpha,\alpha'$ -dibromoxylene,  $\text{Cu(I)Br}$  was used in an amount of  $1.47 \times$

10<sup>-5</sup> mol, and Bpy was present in a molar amount of  $4.5 \times 10^{-5}$  mol. The polymerization was conducted at 100°C for 15 h. The polymer was obtained in 95% yield. The  $M_{n,SEC}$  of 29,500 was in very good agreement with the  $M_{n,th.}$  of 31,000. The obtained polymer had an  $M_w/M_n$  of 1.15.

5  
5/1  
BB  
✓  
10  
15  
20  
30  
40  
50  
60  
70  
80  
90  
100  
110  
120  
130  
140  
150  
160  
170  
180  
190  
200  
210  
220  
230  
240  
250  
260  
270  
280  
290  
300  
310  
320  
330  
340  
350  
360  
370  
380  
390  
400  
410  
420  
430  
440  
450  
460  
470  
480  
490  
500  
510  
520  
530  
540  
550  
560  
570  
580  
590  
600  
610  
620  
630  
640  
650  
660  
670  
680  
690  
700  
710  
720  
730  
740  
750  
760  
770  
780  
790  
800  
810  
820  
830  
840  
850  
860  
870  
880  
890  
900  
910  
920  
930  
940  
950  
960  
970  
980  
990  
1000  
1010  
1020  
1030  
1040  
1050  
1060  
1070  
1080  
1090  
1100  
1110  
1120  
1130  
1140  
1150  
1160  
1170  
1180  
1190  
1200  
1210  
1220  
1230  
1240  
1250  
1260  
1270  
1280  
1290  
1300  
1310  
1320  
1330  
1340  
1350  
1360  
1370  
1380  
1390  
1400  
1410  
1420  
1430  
1440  
1450  
1460  
1470  
1480  
1490  
1500  
1510  
1520  
1530  
1540  
1550  
1560  
1570  
1580  
1590  
1600  
1610  
1620  
1630  
1640  
1650  
1660  
1670  
1680  
1690  
1700  
1710  
1720  
1730  
1740  
1750  
1760  
1770  
1780  
1790  
1800  
1810  
1820  
1830  
1840  
1850  
1860  
1870  
1880  
1890  
1900  
1910  
1920  
1930  
1940  
1950  
1960  
1970  
1980  
1990  
2000  
2010  
2020  
2030  
2040  
2050  
2060  
2070  
2080  
2090  
2100  
2110  
2120  
2130  
2140  
2150  
2160  
2170  
2180  
2190  
2200  
2210  
2220  
2230  
2240  
2250  
2260  
2270  
2280  
2290  
2300  
2310  
2320  
2330  
2340  
2350  
2360  
2370  
2380  
2390  
2400  
2410  
2420  
2430  
2440  
2450  
2460  
2470  
2480  
2490  
2500  
2510  
2520  
2530  
2540  
2550  
2560  
2570  
2580  
2590  
2600  
2610  
2620  
2630  
2640  
2650  
2660  
2670  
2680  
2690  
2700  
2710  
2720  
2730  
2740  
2750  
2760  
2770  
2780  
2790  
2800  
2810  
2820  
2830  
2840  
2850  
2860  
2870  
2880  
2890  
2900  
2910  
2920  
2930  
2940  
2950  
2960  
2970  
2980  
2990  
3000  
3010  
3020  
3030  
3040  
3050  
3060  
3070  
3080  
3090  
3100  
3110  
3120  
3130  
3140  
3150  
3160  
3170  
3180  
3190  
3200  
3210  
3220  
3230  
3240  
3250  
3260  
3270  
3280  
3290  
3300  
3310  
3320  
3330  
3340  
3350  
3360  
3370  
3380  
3390  
3400  
3410  
3420  
3430  
3440  
3450  
3460  
3470  
3480  
3490  
3500  
3510  
3520  
3530  
3540  
3550  
3560  
3570  
3580  
3590  
3600  
3610  
3620  
3630  
3640  
3650  
3660  
3670  
3680  
3690  
3700  
3710  
3720  
3730  
3740  
3750  
3760  
3770  
3780  
3790  
3800  
3810  
3820  
3830  
3840  
3850  
3860  
3870  
3880  
3890  
3900  
3910  
3920  
3930  
3940  
3950  
3960  
3970  
3980  
3990  
4000  
4010  
4020  
4030  
4040  
4050  
4060  
4070  
4080  
4090  
4100  
4110  
4120  
4130  
4140  
4150  
4160  
4170  
4180  
4190  
4200  
4210  
4220  
4230  
4240  
4250  
4260  
4270  
4280  
4290  
4300  
4310  
4320  
4330  
4340  
4350  
4360  
4370  
4380  
4390  
4400  
4410  
4420  
4430  
4440  
4450  
4460  
4470  
4480  
4490  
4500  
4510  
4520  
4530  
4540  
4550  
4560  
4570  
4580  
4590  
4600  
4610  
4620  
4630  
4640  
4650  
4660  
4670  
4680  
4690  
4700  
4710  
4720  
4730  
4740  
4750  
4760  
4770  
4780  
4790  
4800  
4810  
4820  
4830  
4840  
4850  
4860  
4870  
4880  
4890  
4900  
4910  
4920  
4930  
4940  
4950  
4960  
4970  
4980  
4990  
5000  
5010  
5020  
5030  
5040  
5050  
5060  
5070  
5080  
5090  
5100  
5110  
5120  
5130  
5140  
5150  
5160  
5170  
5180  
5190  
5200  
5210  
5220  
5230  
5240  
5250  
5260  
5270  
5280  
5290  
5300  
5310  
5320  
5330  
5340  
5350  
5360  
5370  
5380  
5390  
5400  
5410  
5420  
5430  
5440  
5450  
5460  
5470  
5480  
5490  
5500  
5510  
5520  
5530  
5540  
5550  
5560  
5570  
5580  
5590  
5600  
5610  
5620  
5630  
5640  
5650  
5660  
5670  
5680  
5690  
5700  
5710  
5720  
5730  
5740  
5750  
5760  
5770  
5780  
5790  
5800  
5810  
5820  
5830  
5840  
5850  
5860  
5870  
5880  
5890  
5900  
5910  
5920  
5930  
5940  
5950  
5960  
5970  
5980  
5990  
6000  
6010  
6020  
6030  
6040  
6050  
6060  
6070  
6080  
6090  
6100  
6110  
6120  
6130  
6140  
6150  
6160  
6170  
6180  
6190  
6200  
6210  
6220  
6230  
6240  
6250  
6260  
6270  
6280  
6290  
6300  
6310  
6320  
6330  
6340  
6350  
6360  
6370  
6380  
6390  
6400  
6410  
6420  
6430  
6440  
6450  
6460  
6470  
6480  
6490  
6500  
6510  
6520  
6530  
6540  
6550  
6560  
6570  
6580  
6590  
6600  
6610  
6620  
6630  
6640  
6650  
6660  
6670  
6680  
6690  
6700  
6710  
6720  
6730  
6740  
6750  
6760  
6770  
6780  
6790  
6800  
6810  
6820  
6830  
6840  
6850  
6860  
6870  
6880  
6890  
6900  
6910  
6920  
6930  
6940  
6950  
6960  
6970  
6980  
6990  
7000  
7010  
7020  
7030  
7040  
7050  
7060  
7070  
7080  
7090  
7100  
7110  
7120  
7130  
7140  
7150  
7160  
7170  
7180  
7190  
7200  
7210  
7220  
7230  
7240  
7250  
7260  
7270  
7280  
7290  
7300  
7310  
7320  
7330  
7340  
7350  
7360  
7370  
7380  
7390  
7400  
7410  
7420  
7430  
7440  
7450  
7460  
7470  
7480  
7490  
7500  
7510  
7520  
7530  
7540  
7550  
7560  
7570  
7580  
7590  
7600  
7610  
7620  
7630  
7640  
7650  
7660  
7670  
7680  
7690  
7700  
7710  
7720  
7730  
7740  
7750  
7760  
7770  
7780  
7790  
7800  
7810  
7820  
7830  
7840  
7850  
7860  
7870  
7880  
7890  
7900  
7910  
7920  
7930  
7940  
7950  
7960  
7970  
7980  
7990  
8000  
8010  
8020  
8030  
8040  
8050  
8060  
8070  
8080  
8090  
8100  
8110  
8120  
8130  
8140  
8150  
8160  
8170  
8180  
8190  
8200  
8210  
8220  
8230  
8240  
8250  
8260  
8270  
8280  
8290  
8300  
8310  
8320  
8330  
8340  
8350  
8360  
8370  
8380  
8390  
8400  
8410  
8420  
8430  
8440  
8450  
8460  
8470  
8480  
8490  
8500  
8510  
8520  
8530  
8540  
8550  
8560  
8570  
8580  
8590  
8600  
8610  
8620  
8630  
8640  
8650  
8660  
8670  
8680  
8690  
8700  
8710  
8720  
8730  
8740  
8750  
8760  
8770  
8780  
8790  
8800  
8810  
8820  
8830  
8840  
8850  
8860  
8870  
8880  
8890  
8900  
8910  
8920  
8930  
8940  
8950  
8960  
8970  
8980  
8990  
9000  
9010  
9020  
9030  
9040  
9050  
9060  
9070  
9080  
9090  
9100  
9110  
9120  
9130  
9140  
9150  
9160  
9170  
9180  
9190  
9200  
9210  
9220  
9230  
9240  
9250  
9260  
9270  
9280  
9290  
9300  
9310  
9320  
9330  
9340  
9350  
9360  
9370  
9380  
9390  
9400  
9410  
9420  
9430  
9440  
9450  
9460  
9470  
9480  
9490  
9500  
9510  
9520  
9530  
9540  
9550  
9560  
9570  
9580  
9590  
9600  
9610  
9620  
9630  
9640  
9650  
9660  
9670  
9680  
9690  
9700  
9710  
9720  
9730  
9740  
9750  
9760  
9770  
9780  
9790  
9800  
9810  
9820  
9830  
9840  
9850  
9860  
9870  
9880  
9890  
9900  
9910  
9920  
9930  
9940  
9950  
9960  
9970  
9980  
9990  
10000

Example 12:

Poly(methyl methacrylate), PMMA, was prepared according to the procedure of Example 3, except that 0.5 g of MMA were used, 0.5 ml of ethyl acetate was employed as a solvent, 2-ethyl bromoisobutyrate ( $2.5 \times 10^{-5}$  mol) was used in place of 1-PECl, Cu(I)Br ( $1.5 \times 10^{-5}$  mol) was used in place of Cu(I)Cl, and Bpy was present in a molar amount of  $4.5 \times 10^{-5}$  mol. The polymerization was conducted at 100°C for 1.5 h. The polymer was obtained in 95% yield. The  $M_{n,SEC}$  of 20,500 was in excellent agreement with the  $M_{n,th.}$  of 19,000. The obtained polymer had an  $M_w/M_n$  of 1.40.

Example 13:

Polyisoprene was prepared according to the procedure of Example 3, except that 0.45 g of isoprene was used in place of St,  $3.77 \times 10^{-5}$  mol of 1-PECl was used,  $3.9 \times 10^{-5}$  mol of Cu(I)Cl was used, and Bpy was present in a molar amount of  $1.2 \times 10^{-4}$  mol. The polymerization was conducted at 130°C for 45 h. The polymer was obtained in 80% yield. The  $M_{n,SEC}$  of 12,700

was in agreement with the  $M_{n,th.}$  of 9,500. The obtained polymer had an  $M_w/M_n$  of 2.0.

Example 14:

5  
10  
A PSt-b-PMA block copolymer was produced according to the procedure of Example 3, except that 0.5 g of PSt-Cl ( $M_n = 4,000$ ,  $M_w/M_n = 1.45$ ) was used in place of 1-PECl as the initiator, 1.0 g of MA was used as the monomer, Cu(I)Cl was present in a molar amount of  $1.25 \times 10^{-4}$  mol and Bpy was present in a molar amount of  $3.75 \times 10^{-4}$  mol. The polymerization was conducted at  $130^\circ\text{C}$  for 5 h. The polymer was obtained in 95% yield. The  $M_{n,SEC}$  of 13,000 was in good agreement with the  $M_{n,th.}$  of 11,600. The obtained polymer had an  $M_w/M_n$  of 1.35.

Example 15:

15  
20  
A PSt-b-PMA-b-PSt triblock copolymer was produced as follows. To a flask equipped with a water condenser and a magnetic stirring bar, the initiator  $\alpha,\alpha'$ -dibromoxylene ( $1 \times 10^{-4}$  mol), CuBr ( $2 \times 10^{-4}$  mol), Bpy ( $6 \times 10^{-4}$  mol), MA (3 g) and EtOAc (10 ml) were added. Argon was then bubbled through the solution, and the solution was heated at  $100^\circ\text{C}$  for 18 h. One ml of solution was withdrawn using a syringe and was analyzed by gas chromatography (GC) and SEC to determine the monomer conversion and  $M_n$ , respectively. PMA was obtained in 100%

yield. The  $M_{n,SEC}$  of 30,500 was in excellent agreement with the  $M_{n,th.}$  of 30,000, and the  $M_w/M_n$  of the PMA was 1.3.

Styrene (1 g) was added to the PMA reaction solution, and the mixture was heated at 100°C for 18 h. The triblock polymer was obtained in 100% yield. The  $M_{n,SEC}$  of 42,000 was in excellent agreement with the  $M_{n,th.}$  of 40,000, and the triblock polymer had an  $M_w/M_n$  of 1.45.

Example 16:

A PMA-b-PSt block copolymer was prepared according to the procedure of Example 3, except that 0.5 g of PMA-Cl ( $M_n = 2,000$ ,  $M_w/M_n = 1.30$ ) was used in place of 1-PECl as the initiator, 1.0 g of MA was used as the monomer, Cu(I)Cl was present in a molar amount of  $2.5 \times 10^{-4}$  mol and Bpy was present in a molar amount of  $7.5 \times 10^{-4}$  mol. The polymerization was conducted at 130°C for 10 h. The polymer was obtained in 90% yield. The  $M_{n,SEC}$  of 11,500 was in excellent agreement with the  $M_{n,th.}$  of 11,000. The obtained polymer had an  $M_w/M_n$  of 1.29.

Example 17:

A random P(St-co-MA) copolymer was prepared according to the procedure of Example 3, except that mixture of MA (0.48 g) and St (0.45 g) was used as comonomers, 1-PECl was used in an amount of 3  $\mu$ L ( $2.26 \times 10^{-5}$  mol), Cu(I)Cl was used in an amount of  $2.22 \times 10^{-5}$  mol and Bpy was present in a molar amount of  $6.5 \times 10^{-5}$  mol. The polymerization was conducted at 130°C for 5 h.

The polymer was obtained in 95% yield. The  $M_{n, SEC}$  of 39,000 was in excellent agreement with the  $M_{n, th.}$  of 39,100. The obtained polymer had an  $M_w/M_n$  of 1.45.

The composition as determined by  $^1H$  NMR contained 48% MA, and 52% St.

Example 18:

A random P(St-co-MMA) copolymer was prepared according to the procedure of Example 17, except that mixture of MMA (0.45 g) and St (0.45 g) was used as comonomers, 1-PEBr (3  $\mu$ L,  $2.2 \times 10^{-5}$  mol) was used in place of 1-PECl, Cu(I)Br ( $2.0 \times 10^{-5}$  mol) was used in place of Cu(I)Cl and Bpy was present in a molar amount of  $4.5 \times 10^{-5}$  mol. The polymerization was conducted at 100°C for 14 h. The polymer was obtained in 90% yield. The  $M_{n, SEC}$  of 38,000 was in excellent agreement with the  $M_{n, th.}$  of 36,900. The obtained polymer had an  $M_w/M_n$  of 1.55.

Example 19:

A six arm star PMA polymer was prepared according to the procedure of Example 3, except that  $C_6(CH_2Br)_6$  ( $1 \times 10^{-4}$  mol) was used in place of 1-PECl, MA (1 ml, 0.96 g) was used as the monomer, CuBr ( $1.8 \times 10^{-4}$  mol) was used in place of Cu(I)Cl, and Bpy was present in a molar amount of  $5.8 \times 10^{-4}$  mol. The polymerization was conducted at 110°C for 45 h. The polymer was obtained in 100% yield. The  $M_{n, SEC}$  of 9,600 was in perfect

agreement with the  $M_{n,th.}$  of 9,600. The obtained polymer had an  $M_w/M_n$  of 2.0.

Example 20:

5 A six-arm star PSt polymer was prepared according to the procedure of Example 3, except that  $1.53 \times 10^{-5}$  mol of  $C_6(CH_2Br)_6$  was used in place of 1-PECl. The polymer was obtained in 90% yield. The  $M_{n,SEC}$  of 24,100 was in close agreement with the  $M_{n,th.}$  of 26,800. The obtained polymer had an  $M_w/M_n$  of 1.25.

10 Example 21:

An end-functional PSt having a COOH end group was prepared according to the procedure of Example 3, except that 2-chloropropionic acid ( $1.74 \times 10^{-5}$  mol) was used in place of 1-PECl, and the reaction was conducted for 14 h. The polymer was obtained in 50% yield, and had an  $M_{n,SEC} = 39,600$  and an  $M_w/M_n = 1.45$ .

Example 22:

20 A telechelic PMMA with two Br end groups was prepared at 100°C in ethyl acetate according to the procedure of Example 3, except that  $1.00 \times 10^{-4}$  mol of  $C_6H_4(CH_2Br)_2$  was used in place of 1-PECl, 0.5 g of MMA was used,  $2.00 \times 10^{-4}$  mol of CuCl was used, and  $5.2 \times 10^{-4}$  mol of Bpy was present. The polymer was obtained in 100% yield after 8 h. The  $M_{n,SEC}$  of 4,800 was in

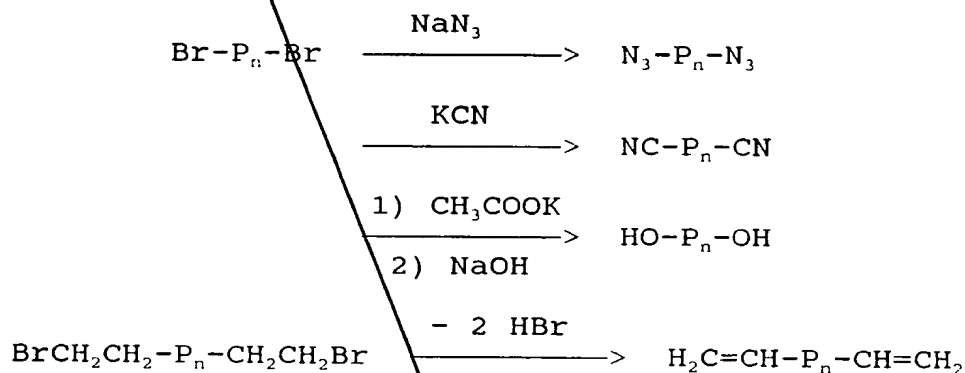
RECEIVED "28TH" 1960

close agreement with the  $M_{n,th.}$  of 5,000. The obtained polymer had an  $M_w/M_n$  of 1.35.

Example 23:

HBr abstraction (by known methods) of the Br-functional PMMA produced in Example 22 can lead to a telechelic (co)polymer with olefinic end groups, from which a telechelic (co)polymer with primary alcohol end groups can be formed by sequential hydroboration/oxidation (by known methods). Nitration/reduction (by known methods) gives the corresponding amine-ended telechelic (co)polymer.

A Br-ended telechelic (co)polymer ("Br- $P_n$ -Br") can be converted to other groups in one or two step as follows:



Example 24:

An end-functional and in-chain functional PSt with two Br end groups and two central Br groups was prepared at 100°C according to the procedure of Example 3, except that  $0.900 \times 10^{-4}$  mol of  $\text{CBr}_4$  was used in place of 1- $\text{PECl}$ , 0.5 g of St was

used,  $1.5 \times 10^{-4}$  mol of CuCl was used, and  $3.2 \times 10^{-4}$  mol of Bpy was present. The polymer was obtained in 90% yield after 20 h. The  $M_{n,SEC}$  of 4,500 was in agreement with the  $M_{n,th.}$  of 5,000. The obtained polymer had an  $M_w/M_n$  of 1.45. The obtained polymer can be converted to any of the other four functional PSt's according to the procedures described in Example 23.

A number of ATRP's of styrene using transition metal complexes other than CuCl/Bpy are summarized in Table 8, and a number of ATRP's of methyl methacrylate using transition metal complexes other than CuCl/Bpy are summarized in Table 9.

00034137.030398



TABLE 8

St ATRP in the Presence of Other Transition Metal Complexes Other Than CuCl / Bpy

Initiator	Mt	L	Temp.	time	conv.	Mn,th	Mn,SEC	Mw/Mn
M	M	M	°C	h				
AIBN	CuCl <sub>2</sub>	Bpy	130	3.5h	0.85	7500	6100	2.7
0.11M	0.076M	0.38						
1-PECl	FeCl <sub>2</sub>	(EtO) <sub>3</sub> P	130	5.5	0.85	21100	19300	3.1
0.075M	0.075	0.375						
1-PECl	CuCl/CuCl <sub>2</sub>	Bpy	130	21	0.80	95500	72500	1.45
0.0075M	0.0075M/"	0.038M						
AIBN	CuCl <sub>2</sub>	bpy	130	21	0.90	25000	18500	1.8
0.034M	0.06	0.14						
AIBN			130	21	0.6		544000	4.50
0.034								
1-PECl	RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>		130	13	0.9	18400	18300	2.2
0.044M	0.037M							

TABLE 9

MMA ATRP in the Presence of Other Transition Metal Complexes Other Than CuCl / Bpy

Initiator	Mt	L	Temp.(°C)	time	conv.	Mn,th	Mn,SEC	Mw/Mn
(M)	(M)	(M)		hr				
2-ClEPN	FeCl <sub>2</sub>	PPh <sub>3</sub>	130	5	0.85	8460	63100	2.1
0.047M	0.021M	0.073						
"	FeCl <sub>2</sub>	PPh <sub>3</sub>	130	5	0.80	8000	65100	1.8
	0.042	0.14						
"	FeCl <sub>2</sub>	PPh <sub>3</sub>	130	5	0.85	8500	38600	1.76
	0.047	0.28						
"	FeCl <sub>2</sub>	PPh <sub>3</sub>	130	5	0.90	8700	71700	2.1
	0.084	0.3						